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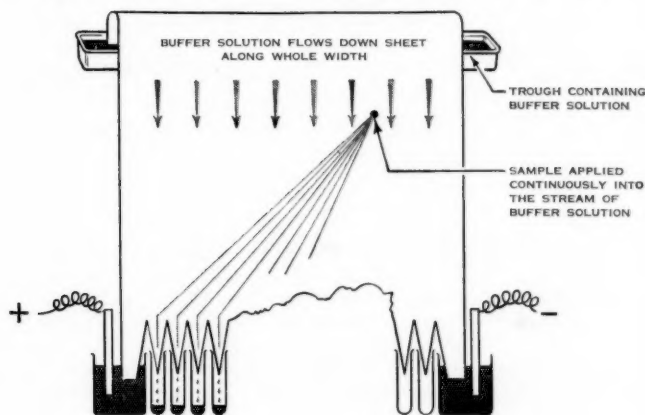
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ANALYTICAL ABSTRACTS

PROGRESS IN CHROMATOGRAPHY 3



CONTINUOUS ELECTROPHORESIS

In our previous advertisement we discussed the separation of large molecules and colloidal particles by making use of the electric charge which most of these carry. We showed how the technique of electrophoresis can be combined with the sensitivity, speed and stability of chromatographic methods. Above, we show an arrangement whereby separation is continuous, the fractions being collected in separate vessels. The sheet of specially cut filter paper (pattern CE/1) hangs vertically, and is saturated by the conducting buffer solution. The direction of migration of any component is determined by the rates at which it travels in the descending buffer and in the electric field between the electrodes. The components therefore diverge and are collected in vessels placed at appropriate points.

SEPARATION OF AMINO ACIDS

An interesting application of continuous electrophoresis is the separation of amino acids, either into groups (acidic, neutral and basic) or into individual amino acids, depending on the pH of the acetic acid used as buffer.

Having a high charge, the particles migrate rapidly towards one or other of the electrodes and this must be balanced by selecting a paper with a correspondingly high rate of downward flow.

The basic group migrates as a whole towards the cathode; the neutral group also moves towards the cathode, but very slightly; the acid group migrates towards the anode, and also separates into individual amino acids. Further separation of neutral and basic groups is achieved by changing the pH of the acetic acid buffer.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2606. Gravimetric, volumetric and absorptiometric analysis. F. J. Bryant (Atomic Energy Authority, Woolwich, England). *Research*, 1956, 9, 50-54.—Recent developments in analytical methods, notably the estimation of a constituent by selective light-absorption measurements and the use of complexing and chelating agents, are reviewed. (23 references.) S. C. I. ABSTR.

2607. Ultramicro-analysis: past, present and future. C. L. Wilson (Queen's Univ., Belfast). *Mikrochim. Acta*, 1956, (1-3), 91-103.—The theoretical limits of sample size for quant. analysis have been calculated at about 10^{-16} g. Ultramicro-analysis is arbitrarily defined as quant. operations carried out on samples of 10^{-8} g or 10^{-3} ml, although radioactivation, for example, enables measurement down to 10^{-13} g to be readily accomplished. Operations of weighing and titration in the ultramicro range are reviewed. Adaptation of classical procedures to the ultramicro scale for use as referee methods for existing colorimetric and radiometric microgram techniques is advocated. A tenfold increase in sample size up to 10^{-4} g might do much to encourage the use of ultramicro-analysis and greater accuracy would be achieved.

D. F. PHILLIPS

2608. Precautionary measures in precision weighing. A. A. Benedetti-Pichler (Queens Coll., Flushing 67, New York). *Mikrochim. Acta*, 1956, (1-3), 565-576.—In order to attain the highest precision inherent in a given balance the following rules are recommended. (1) The weight of the object should be almost completely counterbalanced with suitable weights and tares, the residual weight difference being then determined from the inclination of the beam. (2) Instead of direct weighing, the Gauss transposition method should be used, as this procedure halves the standard deviation of the observed weight. (3) Calibrated weights should be used in suitably limited numbers, and their corrections to true weight applied. These corrections must be determined by a suitable technique. (4) Tares are so chosen that their volume is almost equal to that of the object being weighed. (5) The weight of the balance rider should not be more than 10^3 times the standard deviation of the instrument indication. (6) The rest-point is best computed from observations of the reversal points of the swinging pointer. The rider position should be so chosen that the instrument indication (deflection \times value of one division of pointer scale) is \geq six-tenths of one division of the rider scale.

D. F. PHILLIPS

2609. Systematic investigations on the application of diethylthiocarbamate in analysis. H. Bode. A.E.R.E. Lib/Trans 604, 22 pp.—This is a translation into English of papers published by the

author in *Z. anal. Chem.*, 1955, 144 (3), 165 (cf. *Anal. Abstr.*, 1955, 2, 258, 1207 and 1750). N. E.

2610. Analytical reactions of 2-mercaptoreosorcinol. V. M. Dziomko and A. I. Cherepakhin. *Sbornik Statei Vses. Zaach. Politekh. Inst.*, 1955, (9), 65-69; *Ref. Zhur., Khim.*, 1955, Abstr. No. 46,097.—The reaction of 2-mercaptoreosorcinol with a large number of inorganic ions, some of which give characteristic colorations, is studied. In certain cases the colours obtained are deeper than those given by pyrogallol.

G. S. SMITH

2611. Co-precipitation [of inorganic cations and anions] in reactions with organic reagents. I. M. Korenman. *Zavod. Lab.*, 1956, 22 (2), 146-154.—A review with 113 references.

G. S. SMITH

2612. Water repellency of silicone on microburette tips. M. H. Pugh (Nat. Inst. of Dental Res., U.S. Dept. Health, Educ. and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part 1), 557.—Rigid control of the size of droplets from a Koch microburette is desirable. Occasionally drops fail to hang freely and tend to form by creeping upward away from the orifice, owing to the hydrophilic nature of glass. This can be remedied by drying the end of the tip with cleansing tissue and immediately rubbing it with a silicone-treated tissue so as to render the surface on the ground point of the tip hydrophobic. After this treatment individual volumes of about 0.0001 ml can be delivered easily.

K. A. PROCTOR

2613. Solvent removal by vacuum evaporation. N. S. Radin (Veterans Admin. Res. Hosp. & N.W. Univ. Med. School, Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part 1), 542-543.—The removal of volatile solvents without loss of solute by vacuum distillation is described. Bumping is prevented by imparting a swirling action to the soln. A variety of containers can be employed, including 10 test-tubes used simultaneously, Erlenmeyer flasks (< 125 ml), flat-bottomed flasks (< 300 ml) and round-bottomed flasks (< 1000 ml). The containers (except the test-tubes) can be more than half filled. With one of the devices described, continuous feeding is possible.

K. A. PROCTOR

2614. Particle-size distribution and number of particles per unit mass of some fluorescent powders. J. Rosinski, H. E. Glaess and C. R. McCully (Illinois Inst. of Technol., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part 1), 486-490.—Dispersions of fluorescent particles offer a convenient method of tracing the movement of air parcels over long distances and of studying the behaviour of aerosols under laboratory or field conditions. Measurement of particle-size distribution and of the number of particles per unit mass appeared to be unsatisfactory by conventional methods, and two new techniques, dilution - microscopic and dilution - photometric, are described.

The dilution - microscopic method involves photographing all particles under investigation and is used to classify the tracer when collected particles have to be sized and counted. The dilution - photometric method, based on the fact that the intensity of fluorescent light *vs.* the number of particles gives a straight line, is used to determine rapidly the total number of collected particles.

K. A. PROCTOR

2615. Potassium (meta)periodate as a volumetric reagent. VI. Bromimetric method. R. C. Paul and A. Singh (Dept. Chem., Punjab Univ. Coll., Hoshiarpore, India). *J. Indian Chem. Soc.*, 1955, **32** (11), 736-738.—Potassium periodate, KIO_4 , is used with KBr for determining substances oxidised with difficulty. *Procedure*—The reducing substance to be estimated and 30 to 40 ml of water are put into a conical flask and KBr (1 g) and HCl (1:1) (20 ml) are added. A measured excess of 0.1 N KIO_4 (30 to 40 ml) is added and the flask is corked and left for 5 to 10 min. in cold water to complete the oxidation. Starch soln. is added followed by standard As_2O_3 solution in portions of 0.5 to 1 ml, until the solution is permanently dark brown. Ten ml of 0.5 N KCN are then added and the solution is allowed to stand until a blue colour appears. The solution is then titrated very slowly, with constant shaking, against 0.1 N KIO_4 . Results are given for K Sb tartrate, hydrazine sulphate, FeSO_4 , KCN, $\text{Na}_2\text{S}_2\text{O}_3$, KSCN, H_2SO_3 , $\text{Na}_2\text{S}_4\text{O}_6$, SnCl_2 and $\text{K}_4\text{Fe}(\text{CN})_6$. The equations for the various reactions are given. E. J. H. BIRCH

2616. Cerimetry. II. Cerimetric titrations in presence of fluoride. I. Lange and A. Petzold (Bergakad. Freiberg, Sachsen, Germany). *Z. anal. Chem.*, 1956, **150** (1), 24-29.—Interference by F^- during cerimetry, which leads to a high consumption of Ce^{IV} , is discussed, and the possible formation of CeF_4 or complex fluorocerates is mentioned. Interference by F^- is avoided by the addition of H_3BO_3 and formation of BF_4^- . Silicic acid is unsuitable as a complexing agent for F^- in cerimetry as it adsorbs the indicator. The H_3BO_3 complexing method is illustrated for the cerimetric determination of Fe^{II} , As^{III} , I^- and $\text{S}_2\text{O}_3^{2-}$, with ferroin or starch - I indicators; high accuracy is achieved. This method is of special importance in the analysis of silicate minerals. J. P. STERN

2617. Chelatometry. VII. The problem of buffering. Use of hexamine and of chloroacetic acid for compleximetric titrations. P. Wehber (Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, **149** (6), 419-432.—Since the commonly used buffers often form metal complexes, and thus interfere with chelatometry, other buffers are examined. The use of chloroacetic acid buffer at pH 2 enables FeCl_3 to be titrated at 50° to 60° C with 0.1 M nitrilotriacetic acid (NTA), with Chromazurol S as indicator, with high accuracy. Hexamine - HCl buffer (I) (pH 5.5 to 6) is used in the titration of CuCl_2 with NTA or EDTA (disodium salt), with murexide indicator, and obviates the difficulties experienced with murexide in the presence of NH_3 . Alternatively, I (pH 5.5 to 6) facilitates the titration of CuCl_2 with NTA, with Chromazurol S as indicator, the end-point of which is indistinct in the presence of excess of acetate. I also makes possible the titration at pH 5.0 to 5.5 of CuCl_2 with NTA, with Variamine blue B indicator, which is impossible in acetate buffer. In each of these determinations the accuracy is very high.

Details of interfering ions for each indicator system are given. J. P. STERN

2618. New theory of adsorption indicators. p-Ethoxychrysoidine as an adsorption indicator. E. Pungor and E. Schulek (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Z. anal. Chem.*, 1956, **150** (3), 166-178.—p-Ethoxychrysoidine is known to be a suitable adsorption indicator for the determination of I^- , but it differs from other similar indicators in not showing a large change in adsorption at the end-point. Experiments have been carried out on the adsorption of indicators on to silver halide surfaces which have led to the replacement of Fajans's theory by a new theory of adsorption indicators. The physico-chemical constants of the adsorbed indicator depend on the nature and amount of the ions adsorbed on to the surface of the ppt. The change of one of these constants (which one must be decided for each indicator) at the end-point of the titration causes a change in colour. When p-ethoxychrysoidine is used in the determination of I^- , the indicator undergoes an acid - base change at the end-point. In the presence of an excess of I^- , adsorbed I^- attract protons so that the indicator assumes the acid form, leaving the soln. alkaline. In the presence of an excess of Ag^+ , adsorbed Ag^+ expel protons so that the indicator assumes the alkaline form whilst the soln. becomes acid.

J. H. WATON

2619. p-Ethoxychrysoidine as an acid - base and redox indicator. E. Pungor and E. Schulek (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Z. anal. Chem.*, 1956, **150** (3), 161-166.—From the extinction curves of p-ethoxychrysoidine at various pH values, a mechanism is suggested for the colour changes that occur when this compound is used as an acid - base indicator. The formation of quaternary ammonium bases is considered to take place. When used as a redox indicator, p-ethoxychrysoidine is oxidised to an azoxy product. The redox potential is 0.76 V when measured against a normal hydrogen electrode.

J. H. WATON

2620. Inorganic paper-chromatography. M. Lederer (Inst. du Radium, Paris). *Mikrochim. Acta*, 1956, (1-3), 43-53.—The numerous publications dealing with inorganic chromatography now permit certain important general principles to be recognised. Inorganic paper separations can be divided on a chemical basis into three main groups—(1) separation with solvents containing strong acids, bases or complexing reagents; (2) separation under what may be termed 'non-equilibrium' conditions. Each group can be subdivided into two parts according to the polarity of the solvent. The mechanism of each group is examined and examples are quoted. The second part of the paper deals with several new types of separation and solvents. These include the behaviour of Se^{IV} and Te^{IV} in a variety of solvents, and a very clean separation of 0.05 per cent. of ^{134}Cs from ^{86}Rb , the solvent being phenol saturated with 2 N HCl. Finally the R_F values of a number of ions have been measured by means of butanol saturated with H_2SO_4 or H_3PO_4 as solvent. D. F. PHILLIPS

2621. Use of ion exchangers in analytical chemistry. VII. Possibility of quantitative separation and application to practical problems. D.

Jentzsch (Forschungsinst. f. Nichtedle-Metalle, Freiberg, Germany). *Z. anal. Chem.*, 1956, **150** (4), 241-250.—The influence of particle size on the affinity of the ion-exchange bed for ions is discussed and an increase in affinity with diminishing particle size is demonstrated. For optimum separation of two cations, e.g., Al and Fe^{III}, or Fe and In, the use of fine particles (50 per cent. of which have a diameter between 0.06 to 0.08 mm, and the rest < 0.06 mm) is advocated in simple filter-beds. By consideration of the elution const. of a variety of cations, a table is constructed which shows the probability of separation of binary mixtures of metal ions. The technique is applied to the determination of Cu, Zn and Pb in electro-nickel, which is achieved in 6 to 6.5 M HCl on Wofatit L 150. To avoid interference, any Fe^{III} present is reduced to Fe^{II} and any Co is removed. Similarly, Ga may be quant. separated from an excess of Sn^{IV} in 4 M HCl, when Ga is eluted first. J. P. STERN

2622. **Micro-electrophoresis.** H. Michl (Chem. Lab., Univ. of Vienna). *Mikrochim. Acta*, 1956, (1-3), 54-70.—A review is given of the techniques and applications of free and zone electrophoresis. Free electrophoresis is illustrated by a description of the method of Svensson, whilst the apparatus of Antweiler exemplifies the micro scale. For zone electrophoresis the emphasis is mainly on paper techniques. (79 references.) D. F. PHILLIPS

2623. **Detection limits in spectrochemical analysis.** H. de Laffolie (Inst. Phys. Chem., Univ. Münster, Germany). *Mikrochim. Acta*, 1956, (1-3), 304-310.—The limit of detection of an element is governed by the point at which the spectral line of the element emerges from the continuous background radiation emitted by the light source. In direct-reading equipment such as the Quantometer this background radiation appears as electronic noise in the photomultiplier; in photographic recording, as plate background. Emulsion characteristics which determine the emergence of line from background are graininess and the value of γ . The author shows that by the use of Seidel-transformed densities the line to background relationship at detection limits of an element can be evaluated. Numerical values of this relationship for eight widely used emulsions are tabulated at 4300, 3500 and 2800 Å. The higher the wavelength the more favourable is the relationship because the characteristic curve is steeper. D. F. PHILLIPS

2624. **Application of mass spectroscopy to analytical chemistry.** H. Hintenberger (Max Planck Inst. Chem., Mainz, Germany). *Mikrochim. Acta*, 1956, (1-3), 71-90.—The necessary equipment is briefly described and applications are discussed with special reference to the use of micro samples. The technique lends itself most readily to gas analysis or to substances which can be converted to the gaseous form. Analysis of solid substances, although less well developed, can be achieved through complete volatilisation of the sample in a high-frequency spark. Examples include determination of chromium and nickel in alloy steels, and light-element impurities in uranium metal. Limits of detection can be increased by a factor of from 100 to 1000 by means of secondary emission amplification. Finally the advantages of dilution techniques with separated stable isotopes are indicated. D. F. PHILLIPS

2625. **Applications of radioactivity in analytical chemistry.** H. Götte (Max Planck Inst. Chem., Mainz, Germany). *Mikrochim. Acta*, 1956, (1-3), 27-42.—The origin, principles and advantages of radioactive tracer, "correction" and radioactivation analytical procedures are discussed. Examples of their application to both organic and inorganic problems are given. The present-day availability of artificial radio-isotopes together with the high sensitivity, specificity and versatility of the techniques has a significance for microchemistry at least equal to that of colorimetry. D. F. PHILLIPS

2.—INORGANIC ANALYSIS

2626. **The analytical application of -onium compounds. IX. Polarographic behaviour of triphenylsulphonium chloride towards several metal ions.** Mutsuaki Shinagawa, Hiroshi Matsuo and Nobufumi Maki (Chem. Dept., Faculty of Sci., Hiroshima Univ., Higashisenda-machi, Hiroshima). *Japan Analyst.*, 1956, **5** (2), 80-83.—In 0.1 M KCl soln. triphenylsulphonium chloride (I) gives a two-step wave at -1.5 V vs. the S.C.E., with a max. which is suppressed by non-ionic surfactants such as polyoxyethylene sorbitan mono-oleate or dodecyltrimethylammonium chloride. The first wave is independent of pH, whilst the second one is dependent on pH. The height of the first wave or the sum of both waves is proportional to the concn. ($< 5 \times 10^{-4}$ M). I reacts with heavy metals, including Hg, Bi, Cd, Sb and Sn, in KI, KCN or KSCN soln. The reaction with Hg and Bi is sufficiently quant. to be utilised for the amperometric determination of both metals. The accuracy is within 1 per cent. K. SAITO

2627. **Semi-quantitative spectrographic analysis in mineralogical and geochemical studies.** L. N. Indichenko. *Doklady Akad. Nauk SSSR*, 1955, **100** (4), 775-778; *Ref. Zhur., Khim.*, 1955, Abstr. No. 49,126.—For determining contents of elements within the range 0.005 to 10 per cent. the tabulation of the dependence of line intensities on concn. as found by the use of standards of composition similar to that of the samples is recommended. Spectra are excited by means of a d.c. arc and photographed in a medium spectrograph. In analysing samples the spectra of the standards are not photographed. In sulphide minerals sensitivities of many determinations are greater than in silicate minerals. G. S. SMITH

2628. **Effect of viscosity of solvent on the polarographic diffusion currents of ions of metals.** Ya. I. Turyan and P. A. Vysokii (Kishinev State Univ., USSR). *Dokl. Akad. Nauk SSSR*, 1955, **103** (6), 1053-1055.—The expression $K_s \sqrt{\eta} = A' + B'/\sqrt{\eta}$ is shown to hold for Zn, Cu^{II}, Ti^{IV}, Cd and Pb^{II} ions in 0 to 87 per cent. v/v of glycerol. R. TRUSCOE

2629. **Influence of methanol on the determination of water with Karl Fischer solution.** E. Eberius and W. Kowalski (Zinkindustrie A.-G., Duisburg-Hamborn, Germany). *Z. anal. Chem.*, 1956, **150** (1), 13-20.—It is confirmed that the end-point of normal Karl Fischer titrations depends on the water to methanol ratio (*cf.* Bonauguri and Seniga, *Anal. Abstr.*, 1955, **2**, 1756). The reaction of methanol with the reagent is inhibited by one of

the reaction products, so that titration of water added to aq. methanol that has already been titrated affords correct results. Since errors are minimised if the water content is determined by difference (especially if the vol. of methanol used are similar), many determinations of small amounts of water give results correct to within normal experimental error.

J. P. STERN

2630. Determination of alkalis in silicates. E. Zymny. *Glas-Email-Keramo-Tech.*, 1955, **6**, 236-237.—After the silicate has been decomposed with CaCO_3 and the water-sol. components dissolved and separated by filtration, the filtrate is acidified with acetic acid and K is determined as $\text{KB}(\text{C}_6\text{H}_5)_4$, either gravimetrically by the method of Raff and Brotz (*Z. anal. Chem.*, 1951, **133**, 241) or by titrating an acetone soln. of the ppt. with AgNO_3 . Only small quantities of acetone (> 10 ml per 25 mg of K) can be used, to avoid excessive soln. of the silver salt. For each 10 ml of acetone, 5 ml of 2 N acetic acid, 1 ml of 0.1 N KBr and two drops of eosin soln. (1 per cent.) are added and titrated with 0.05 N AgNO_3 to the colour change; KBr makes the end-point sharper. The total vol. of AgNO_3 soln. added should not be greater than the vol. of acetone, or the $\text{KB}(\text{C}_6\text{H}_5)_4$ may be pptd. before being titrated. Sodium can be determined by the Zn uranyl acetate method.

CHEM. ABSTR.

2631. The reaction between lithium and 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (thoron). L. P. Adamovich and T. T. Alekseeva. *Uch. Zap. Kharkov. Univ.*, 1954, **54**; *Trudy Khim. Fak. i Nauch. Issledovatel. Inst. Khim.*, **12**, 209-214; *Ref. Zhur.*, *Khim.*, 1955, (15), Abstr. No. 31,855.—A study of the composition of the compound formed by the interaction of Li with 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (I) was carried out by Ostromyslenskii's method with the help of the organic-logarithmic method. At pH 13.5, Li and I combine in the ratio 1:1. The dissociation constant was found to be $(2.4 \pm 0.3) \times 10^{-3}$, and the coeff. of mol. extinction at 470 m μ was $10,680 \pm 80$. The minimum amount detectable with an accuracy of 98 per cent. is 50 mg per ml. (See also *Anal. Abstr.*, 1956, **3**, 2646, 2695.)

C. D. KOPKIN

2632. The spectrographic determination of lithium in aluminium metal. F. T. Birks (A.E.R.E., Harwell, England). A.E.R.E. Publication C/R 196, 1955, 7 pp.—Lithium in the range 5 to 500 p.p.m. is determined by converting the sample into its oxide and applying the carrier distillation method due to Scribner and Mullin. Sodium chloride is used as the carrier. Quantitative results are obtained by the use of synthetic standards and direct comparison of the line density or width of Li 6103.6 Å.

P. T. BEALE

2633. A spectral method for the determination of sodium in aluminosilicates. S. N. Aleksandrov, G. P. Malakhova and Ya. E. Shmulyakovskii. *Neftyanoe Khoz.*, 1954, (12), 64-67; *Ref. Zhur.*, *Khim.*, 1955, (17), Abstr. No. 37,490.—The sample (0.05 to 0.25 per cent. of Na_2O), ground to a powder, is mixed with BaCO_3 (1:3) to eliminate ejection of the sample from the electrode and to ensure complete vaporisation of the Na, and placed in a cavity (about 2.5 mm \times 2.5 mm) in the lower angular electrode of the quartz spectrograph ISP-22, with an a.c. arc generator PS-39 (7 to

8 amp.). The photographic conditions are—width of slit, 0.015 mm; inter-electrode distance, 3 mm; height of diaphragm of three-lens condenser, 5 mm; and exposure, 40 sec.; the photographic plates are spectral plates, type I. The line used for analysis is Na 3302.3 Å, with the dense background around this line as internal standard. On the same plate are photographed the spectra of standards prepared by the addition of known amounts of Na_2CO_3 soln. to an aluminosilicate ignited at 750° C for 2 hr., and freed from Na by boiling with 1 per cent. HCl for 5 to 7 min. The Na_2O remaining (0.05 per cent.) is determined by the method of additions described earlier [Prokofiev; *Izvest. Akad. Nauk SSSR, Ser. Fiz.*, 1954, **14** (6), 660]. The concn. of Na_2O in the sample is determined by comparison with three standards. The standard deviation is ± 10 per cent. Zinc interferes.

C. D. KOPKIN

2634. Spectrographic determination of rubidium and strontium in mica. J. M. López de Azcona (Inst. Geol. y Miner. Españ., Madrid). *Mikrochim. Acta*, 1956, (1-3), 334-338.—The spectrographic determination of the Sr:Rb ratio is used to determine the age of mica. Prior preparation of the 0.1-g sample is described. Spectrography is carried out on a Qu 24 instrument (Zeiss medium dispersion), with a 240 V d.c. arc for which a circuit diagram is given. Spectral lines used are Rb 4201.85 Å and Sr 4077.71 Å. Suitable excitation and calibration procedures are described. The age of the mica is evaluated from the expression— $t = 3.1 \times 10^{11} \times \log_{10} \text{Rb/Sr}$.

D. F. PHILLIPS

2635. Behaviour of traces of caesium revealed by a tracer method with caesium-137. A preliminary study for the determination of caesium in sea water. Noboru Yamagata and Toshiko Yamagata (Kiri Coll. of Tech., Gumma Univ., Tenjin-cho, Kiri). *Japan Analyst*, 1956, **5** (1), 37-40.—The necessary procedures for the separation of traces of Cs from other salts contained in sea water were examined by the use of ^{137}Cs . The separation of alkaline-earth elements by the oxine method and that of SO_4^{2-} by BaCl_2 followed by the pptn. of Ba as BaCO_3 does not involve any appreciable loss of Cs. The separation of other alkalis by the alcohol-ether method results in the loss of only 0.3 per cent. of the total Cs. The concentration of Cs by the HClO_4 , cobaltinitrite or chloroplatinate method, however, results in a significant loss of Cs (> 10 per cent.) when the ratios of Na:K and K:Cs are, respectively, 47 and 200 (the usual ratio in sea water). Jander's process (*Z. anorg. Chem.*, 1929, **179**, 321) for the concentration of Cs with molybdosilicate was also examined and found to be satisfactory. Minami's value for the content of Cs in sea water (0.1 to 1 μg per litre) appears to be reasonable.

K. SAITO

2636. A new microchemical complex and its application to the detection of copper. J. C. Baró Graf (Univ. del Litoral, Rosario, Argentine). *Mikrochim. Acta*, 1956, (1-3), 263-267.—An almost saturated solution of salicylic acid in pyridine forms with Cu a complex which can be used for detection of that element down to a limit of 0.5 μg and at a concn. down to 1 in 10^6 . Topochemical reactions lead the author to conclude that the crystalline compound is a copper-pyridine-salicylate analogous to copper-pyridine-benzoate. The blue-violet compound first formed is soluble in excess of pyridine, giving a violet coloration.

D. F. PHILLIPS

2637. Separation and determination of copper with mercaptoacetic acid. Rokuro Kuroda, Tsuneo Shimizu and Toshi Kawashima (Chem. Inst., College of Sci., Tokyo Univ. of Educ., Otsuka-kubomachi, Tokyo). *Japan Analyst*, 1956, **5** (1), 33-37.—The pptn. of Cu with mercaptoacetic acid (I) in weakly acid soln. was studied with reference to its separation from Pb and Hg. The pptn. is quant. in HNO_3 , H_2SO_4 or acetic acid of pH 3-6 to 6-0 when the amount of I is > 30 times the equiv. of the Cu. In the presence of a comparable amount of Pb or Hg (e.g., Pb, 60 mg; Cu, 30 mg), a large amount of NH_4NO_3 (> 150 times the weight of the Pb or Hg) should be added. No interference results from metals other than Ag and the presence of Cl^- results in low values. For 10 to 100 mg of Cu the accuracy is within 0.5 mg. K. SAITO

2638. Use of catecholsulphonephthalein in colorimetric analysis. III. Photometric determination of copper. M. Svach (Inst. Anal. Chem., Montan-hochschule, Ostrau, Czechoslovakia). *Z. anal. Chem.*, 1956, **149** (6), 417-419.—Catecholsulphonephthalein (catechol violet) forms an intense blue complex (absorption max. at 630 m μ) with Cu in neutral solution. Although suitable for the photometric determination of Cu, this reaction suffers interference from Pb, Ag, Hg, Bi, Sn, Sb, Ni, Zn, Cr, Fe, Mg, Ca, Sr and Ba, and is thus of interest for only pure soln. of Cu. The Beer-Lambert law is obeyed for 100 to 600 μg of Cu in 25 ml of soln., and the colour is fully developed after 15 min. J. P. STERN

2639. Potentiometric non-compensated method for determining copper by means of salicylaldoxime. O. P. Platonova and G. M. Zaitseva. *Zavod. Lab.*, 1956, **22** (2), 165-166.—To determine Cu in aluminium and magnesium alloys and bronzes, the sample (0.25 to 1 g) is dissolved in dil. HCl (1 + 1) [with the addition of a few drops of dil. HNO_3 (1 + 1)], dil. HNO_3 (1 + 1) or aqua regia. The solution is evaporated to a syrup, which is then dissolved in water. The soln., or a suitable aliquot portion (25 ml), is mixed with 15 ml of 20 per cent. ammonium acetate soln. and then with NaCl to saturation. The Cu is titrated potentiometrically with a standard soln. of salicylaldoxime, with tungsten-platinum electrodes. To determine Cu in plating baths, a sample containing 0.01 to 0.03 g of Cu is evaporated with HCl or H_2SO_4 to destroy cyanides, the residue is treated with ammonium acetate and NaCl as described above, and the soln. (120 ml) is titrated with 1 per cent. salicylaldoxime soln. The titrant is prepared by adding dropwise 95 ml of water at 30° C to a soln. of 1 g of salicylaldoxime in 5 ml of ethanol. There is no interference from SO_4^{2-} , Cl^- , NO_3^- , Pb, metastannic acid and small amounts of Fe. G. S. SMITH

2640. Volumetric estimation of copper by the pyridine-thiocyanate complex method. Durga Nath Dhar (H.B. Technol. Inst., Kanpur, India). *J. Inst. Chem., India*, 1955, **27** (4), 262-265.—The volumetric method for the determination of Cu by pptn. with pyridine and a known excess of KSCN and then titrating the excess of KSCN with AgNO_3 (Dobbins *et al.*, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 459) is modified by using a sintered-glass crucible instead of filter-paper for the filtration. After pptn. of the organo-metallic compound, the solution is filtered without dilution to a known vol. (which always leads to some decomposition of the pptd. complex). The rate of filtration and addition of the

solution to be filtered are so adjusted that the liquid does not touch the inside walls of the crucible. The ppt. is not washed. By this procedure errors are kept to a minimum. J. M. JACOBS

2641. Colorimetric determination of copper in lead with diethylammonium diethyldithiocarbamate. K. Lounamaa (Bolidens Gruvaktiebolag, Skelleftehamn, Sweden). *Z. anal. Chem.*, 1956, **150** (1), 7-13.—Diethylammonium diethyldithiocarbamate (I) forms a complex with Cu (Strafford *et al.*, *Analyst*, 1945, **70**, 232) which is extracted from aq. acid by chloroform and is thus suitable for the highly selective colorimetric determination of Cu (> 10 p.p.m.) in Pb. For > 50 μg of Cu, the accuracy is within ± 2 per cent., but Bi (> 100 times the amount of Cu) and Ag (> 3 times) interfere. In the presence of much Bi and of other metals an additional purification step is desirable, but the accuracy for 5 to 50 μg of Cu is still satisfactory. Silver (> 50 μg) interferes and must therefore be removed as AgCl . *Procedure*—For Pb containing only Cu, dissolve the sample (containing 100 to 500 μg of Cu) in HClO_4 and boil to remove all HCl and to clear the soln. Dilute to 3 vol. with water (< 3 N HClO_4) and extract with 10-0 ml of 1 per cent. I in chloroform. Separate the organic phase, determine the extinction at 600 m μ (avoiding any evaporation), and read the content of Cu from the calibration curve. For Pb containing Bi and other metals as well as Cu, dissolve the sample (> 0.5 g of Pb containing 10 to 50 μg of Cu) as described above and dilute the HClO_4 to ≈ 3 N. Extract twice with 5 ml of 0.2 per cent. I in chloroform, separate, and wash the combined organic phase with ≈ 5 per cent. ammonium citrate (pH 9) and 5 per cent. KCN soln. Carefully separate the aq. phase from the chloroform (rejected) and wash it with chloroform. Mix the aq. phase with 3 ml of 40 per cent. formaldehyde soln., add 5 ml of conc. HCl, and extract with 10-0 ml of I in chloroform. Determine the Cu in the extract absorptometrically at 440 m μ . J. P. STERN

2642. Spectrographic analysis of copper-making and lead-making slags for major constituents. N. Lounamaa (Boliden Mining Co., Skelleftehamn, Sweden). *Spectrochim. Acta*, 1956, **7** (6), 358-366.—A method has been developed by which Cu, Pb, ZnO, Al_2O_3 , CaO, FeO, MgO and SiO_2 may be determined spectrographically in the slags obtained from the production of copper and lead alloys. The powdered sample (250.0 ± 2 mg) (≈ 100 mesh) is mixed with a flux (2250 ± 1 mg) of lithium carbonate and boric acid (1:3) and fused in a graphite crucible at 900° C for 5 minutes. Special precautions must be taken for the preparation of the flux, to which are added, as internal standards, Co_3O_4 (10 to 15 per cent.), SnO_2 (0.3 to 1 per cent.) and BeO (0.01 to 0.1 per cent.). The fused metal borates are subjected to a high-voltage spark and the line intensities are recorded photographically. The overall precision of the method is, expressed as coefficient of variation, 1.5 to 3.5 per cent. for the different elements. No systematic errors have been revealed. D. G. HIGGS

2643. The potentiometric and amperometric determination of silver with mercaptophenylthiohydrazolone and mercaptobenzothiazole. M. Malinek and B. Řehák (Metallurgical Lab., Czechoslovak Acad. Sci., Prague). *Z. anal. Chem.*, 1956, **150** (5), 329-333.—Silver solutions can be titrated

potentiometrically with mercaptophenylthiothiadiazolone (I) or mercaptobenzothiazole (II) in neutral or ammoniacal soln. in the presence of EDTA (to prevent the pptn. of ions other than Ag^+), with a silver indicator electrode and a saturated calomel reference electrode. Amperometric determination of Ag^+ with I or II can be carried out in neutral soln. in the presence of EDTA, with a rotating platinum electrode and a Hg - Hg_2Cl_2 half-cell; Hg, Au and some of the platinum metals interfere.

A. R. ROGERS

2644. Qualitative determination of gold by the method of trituration of powders. P. M. Isakov. *Nauch. Byull. Leningrad. Gos. Univ. im. A. A. Zhdanova*, 1955, (33), 27-28; *Ref. Zhur., Khim.*, 1955, Abstr. No. 49,148.—Metallic Au is converted into AuCl_3 by a mixture of NH_4Cl and NH_4NO_3 (2:1), and Au^{+++} are detected by one of the following methods: (i) formation of a dark-brown colloidal soln. by reduction with SnCl_2 and HCl , (ii) formation of red $\text{ZnAu}(\text{SCN})_2$ by addition of NH_4SCN and zinc acetate, (iii) formation of the yellow double-salt, $\text{TiAuCl}_4 \cdot 5\text{H}_2\text{O}$, by salts of Ti, or (iv) formation of benzidine blue by reaction with benzidine.

G. S. SMITH

2645. Analytical chemistry of beryllium. III. A new method of preparing beryllium oxinate dihydrate. Kenji Motojima (Faculty of Eng., Ritsumeikan Univ., Kita-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, 77 (1), 95-97.—A new method for the prep. of crystalline, stoichiometric Be oxinate was devised. A weakly acid soln. of Be (≈ 10 mg in 100 ml) is warmed at 70°C and made ammoniacal to produce a gelatinous ppt. of $\text{Be}(\text{OH})_2$. Oxine soln. (2 g in 100 ml of 5 per cent. acetic acid) is added to the suspension, the beaker being kept on a water bath. A yellow, fine ppt. is gradually formed, which is readily separated on a sintered-glass filter. This ppt. maintains a constant weight between 110° and 180°C , the composition corresponding to $\text{Be}_2\text{O}(\text{C}_{10}\text{H}_8\text{NO})_2 \cdot 2\text{H}_2\text{O}$ (I).

IV. Determination of beryllium with oxine. Kenji Motojima. *Ibid.*, 1956, 77 (1), 97-100.—The use of I for the gravimetric determination of Be was studied. For a quant. prep. of I, freshly pptd. (at pH 7.5 to 9) $\text{Be}(\text{OH})_2$ should be treated with oxine at pH 8.0 ± 0.2 ; this pH adjustment is made by the addition of NH_4Cl (2 g for 100 ml of the sample soln. containing 2 to 20 mg of Be). No interference results from Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ and alkalis; tartrate, ethanol and a large amount of acetate vitiate the estimation.

V. Separation and determination of beryllium with oxine in the presence of aluminium and other metals. Kenji Motojima. *Ibid.*, 1956, 77 (1), 100-102.—Aluminium oxinate is pptd. free from Be with oxine from an acetate buffer of pH 4.5 to 5.2; the ppt. is filtered off and weighed by the usual method. The excess of oxine, which interferes with the precipitation of Be, is removed by extraction with chloroform (20 ml, 4 to 5 times). The aq. layer is treated with NH_4Cl and aq. NH_3 soln. to precipitate $\text{Be}(\text{OH})_2$, which is then dissolved in N HCl (50 ml) and treated as described above. The separation of Be from Fe, Cu and Zn is effected similarly.

K. SAITO

2646. A study of the reaction between beryllium and 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (thoron). L. P. Adamovich and R. S. Didenko. *Uch. Zap. Khar'kov. Univ.*, 1954, 54;

Trudy Khim. Fak. i Nauch. Issledovatel. Inst. Khim., 12, 195-202; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,863.—A study of the composition of the compound formed by the interaction of Be and 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (I) by Ostromyslenskii's method has shown that the constituents react in the ratio 2:3, the ions BeOH^+ and a quinquevalent anion of I taking part. The constant of formation of the complex is $(4.5 \pm 0.4) \times 10^{18}$, and its coeff. of mol. extinction at $480 \text{ m}\mu$ is 46,000. Maximum formation of the complex occurs at pH 12.5.

C. D. KOPKIN

2647. The quantitative determination of magnesium as NaMgF_3 . Sh. T. Talipov and A. T. Tashkhodzhayev. *Trudy Sredneaziat. Gosudarst. Univ. (Tashkent), Khim. Nauk.*, 1954, 55 (7), 141-144; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,500.—The gravimetric method for the determination of Mg (12 to 160 mg) is carried out by pptn. of the magnesium salt in a centrifuge tube with a three-fold excess of NaF, centrifuging the pptd. NaMgF_3 , washing the ppt. with 70 per cent. alcohol, drying it at 130°C , and weighing. The method gives reproducible results, not less accurate than the phosphate and hydroxyquinoline methods, and takes about 3 hr. The error is ± 0.3 per cent.

C. D. KOPKIN

2648. The polarography of magnesium. K. Györfi, L. Poós and J. Prosz (Tech. Univ., Budapest). *Magyar Kém. Foly.*, 1956, 61 (3), 102-106.—By using a special streaming-mercury electrode, clear potential curves were obtained in 0.7 M tetramethylammonium chloride soln. with concentrations of Mg^{++} in the range 3×10^{-3} to $5 \times 10^{-4} \text{ M}$; $E_{\frac{1}{2}} = -2.60 \pm 0.02 \text{ V}$ vs. the S.C.E. The best pH range for polarography is between 5.4 and 6.8. Calcium and particularly lithium interfere; potassium does not.

A. G. PETO

2649. The examination of magnesium compounds with the flame photometer. E. Pungor and I. Konkoly-Thege (Eötvös Loránd Sci. Univ., Inst. Inorg. and Anal. Chem., Budapest). *Magyar Kém. Foly.*, 1956, 61 (1), 17-26.—Various anions and cations interfere with the flame-photometric determination of Mg. Its emission spectrum is independent of the anion present, but the absolute value of the emission depends on the anion because various salts dissociate in the flame, at various velocities, to emitting compounds (MgO or $-\text{MgOH}$). The addition of Cl^- (as HCl) increases the emission, because MgCl_2 hydrolyses rapidly. To correct for the anions present, the unknown soln. and the calibrating solutions should contain the same concn. of the same anions. These can be predicted from the previous chemical treatment of the substance. Alternatively, in each soln. one anion can be kept in a large excess, while keeping the concn. of the others similar to the standard and unknown soln. The interference by Cs, Rb, Na, K and Ca can be calculated by determining the emissions at two wavelengths (350 and $371 \text{ m}\mu$).

A. G. PETO

2650. Flame-photometric determination of calcium in furnace slag. G. W. Standen and C. B. Tennant (The New Jersey Zinc Co., Palmerton, Pa., U.S.A.). *Anal. Chem.*, 1956, 28 (5), 858-860.—A Beckman DU spectrophotometer, fitted with a photomultiplier tube and a Model 9200 flame attachment with an oxy-hydrogen flame, is used for the determination of high contents (≈ 30 per cent.) of Ca. The preparation of solutions for analysis entails (i)

dissolution of the sample, (ii) removal of Fe by pptn. with aq. NH_3 , (iii) dilution to bring the Ca within the required range of 0 to 10 p.p.m., and adjustment of pH. The results are as good as those of a "rapid" chemical method, but are higher than those of a more accurate "slow" chemical method. A correction curve can be plotted.

K. A. PROCTOR

2651. Investigation of the Franke method of determining free calcium hydroxide and free calcium oxide. E. E. Pressler, S. Brunauer and D. L. Kantro (Portland Cement Ass., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 896-902.—An investigation into the Franke ethyl acetoacetate method (*Z. anorg. Chem.*, 1941, **247**, 180) for the determination of uncombined $\text{Ca}(\text{OH})_2$ and CaO in the presence of hydrated and anhydrous substances is described. In a calcium silicate hydrate, in which the Ca was loosely bound, some Ca was found to be removed by this method. A modification is described which gives accurate results for free lime in such substances as Portland cements. The precision of the Franke method was about the same as that of Lerch and Bogue (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 296), but the former is considered to be more rapid and to require less attention during the extraction period. The reagents, although less common than those used in the latter method, are not hazardous in use.

K. A. PROCTOR

2652. Removal of interfering ions by means of oxine in the EDTA titration of calcium and magnesium. Masaaki Akahane and Chikafusa Tanaka (Res. Lab., Japan National Railway Co-op., Shiba-Kaigandori, Minato-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 40-43.—Heavy-metal ions (such as those of Fe^{III} , Mn, Zn, Al, Cd and Ni) that vitiate the EDTA titration of Ca and Mg are removed by pptg. their oxine complexes at a pH of 6.5 to 7. Since an excess of oxine interferes with the titration, it must be removed by extraction with chloroform from a neutral soln. (pH 4.7 to 8.5). The titration of Ca or Mg or their mixture is satisfactorily carried out in the aq. layer (pH 4.8 to 6.5) by the use of Eriochrome black T as indicator. By the addition of ammonium oxalate to the oxine reagent, Ca is pptd. with the oxinates of other metals, whereas Mg remains in the aq. soln. A solid sample (0.1 to 0.2 g) (boiler scale, cement, etc.), is dissolved in 6 N HCl (60 ml) and HClO_4 (1 ml), the soln. is evaporated, then diluted with 0.2 N acetic acid. A suitable portion is treated with Na acetate and oxine (2 per cent. in methanol, 10 ml) and titrated as described above.

K. SAITO

2653. Indicator for titration of calcium in presence of magnesium using disodium dihydrogen ethylenediaminetetra-acetate. H. Diehl and J. L. Ellingboe (Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 882-884.—A new indicator (calcein) for the titration of Ca with EDTA (disodium salt) in the presence of Mg is described. It is prepared by condensing iminodiacetic acid with fluorescein. A sharper end-point is obtained with calcein than with murexide, and the Mg may exceed the Ca by a factor of 20 to 30 without interference. Large amounts of sodium salts do not affect the titration, but Si and Ba interfere and are titrated with Ca. The interference of Cu and Fe can be avoided by the addition of cyanide; Cl^- , NO_3^- , SO_4^{2-} and acetate do not interfere. The titration is performed at pH 12 and the end-point is marked by a

change from yellow - green to brown. The indicator can be added as a solid mixed with 100 pt. of KCl, or as a 2 per cent. NaOH solution, but a better end-point is obtained if some charcoal is present (1 pt. of calcein, 10 pt. of charcoal, 100 pt. of KCl). Calcein can be used for the determination of Ca in water, limestone and other compounds. The standard deviation of replicate determinations on limestone and gypsum samples ranged from ± 0.12 to 0.25 per cent. of the calcium content.

K. A. PROCTOR

2654. Determination of strontium in sea water by using both radioactive and stable isotopes. R. W. Hummel and A. A. Smales (Atomic Energy Res. Estab., Harwell, Berks., England). *Analyst*, 1956, **81**, 110-113.—This work was undertaken to check by independent methods the latest reported values of the Sr content of sea water (Smales, *Brit. Abstr. C*, 1952, 3; Odum, *Science*, 1951, **114**, 211). By an isotope-dilution method with ^{87}Sr , the Sr content of N. Atlantic sea water was found to be 8.0 ± 0.1 mg per litre, and with ^{84}Sr and ^{86}Sr , 8.1 ± 0.1 mg per litre. By a radioactivation method with ^{87}Sr the content was found to be 8.1 ± 0.3 mg per litre, and with ^{86}Sr , 8.05 mg per litre. The details of the techniques used are given. These results agree closely with those obtained recently by flame-photometric methods.

A. O. JONES

2655. The polarographic determination of small amounts of zinc in the presence of much aluminium. I. Bozsai (Chem. Lab., Rákosi Mátyás Works, Budapest). *Magyar Kém. Foly.*, 1956, **62** (4), 139-142.—The polarographic determination of Zn in aq. NH_3 - NH_4Cl soln., in the presence of large amounts of trivalent metals (Al, Fe, Mn), is inaccurate owing to the adsorption of Zn^{++} on the pptd. hydroxides. A loss of ≈ 60 per cent. is caused by $\text{Al}(\text{OH})_3$. The pptn. of the hydroxides is prevented by the addition of complexing agents. The most satisfactory soln. is 0.25 N aq. NH_3 - NH_4Cl containing 1 per cent. sulphosalicylic acid. Zinc has a $E_{1/2}$ of 1.07 V vs. a mercury surface in contact with the soln. In the presence of much Al, the height of the wave decreases; much Mg does not interfere. The Zn can be determined only by the addition method: known amounts of Zn^{++} are added to the unknown soln., and the increase in the height of the step is measured. Saturated Na_2SO_3 soln. is added to remove oxygen, and 0.5 per cent. gelatin is used to decrease the max. The method is suitable for the determination of ≤ 0.01 per cent. of Zn; the accuracy is within ± 1.5 per cent.

A. G. PETO

2656. Chemical analysis of trace elements in biological material. Effect of pH and of salts on the extraction of traces of heavy metals. I. Extraction of zinc with dithizone in carbon tetrachloride. Kin'ya Ogawa (Chem. Dept., Faculty of Sci., Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 144-147.—The extraction of traces of Zn ($< 10 \mu\text{g}$) with CCl_4 soln. of dithizone was examined at various pH values in several different buffer soln. In the pH range 2 to 8, the pH value at which the extraction is completed is increased by the use of a stronger complex-forming agent, such as citrate or tartrate. In the presence of $\text{Na}_2\text{S}_2\text{O}_3$, KCN (masking agent for other heavy-metal ions) or Cl^- , the extraction is so retarded that it is not complete even at pH 6; NO_3^- promote the extraction. When the pH value is > 8 , the extraction proceeds more slowly

irrespective of the ions present; this may be due to a rather strong interaction between Zn and OH⁻.

K. SAITO

2657. The separation of zinc from some other elements by means of anion exchange and solvent extraction and its titrimetric determination with disodium ethylenediaminetetra-acetate. J. A. Hunter and C. C. Miller (Chemistry Dept., The University, Edinburgh 9, Gt. Britain). *Analyst*, 1956, **81**, 79-93.—Previous work (Miller *et al.*, *Anal. Abstr.*, 1954, **1**, 2931) on the separation of Zn from other elements has been extended to include Cd, Ga and In. Zinc is adsorbed from solution in 2 N HCl by the anion-exchange resin Amberlite IRA-400 (Cl); Cd is then fixed on the resin by means of HI and the Zn is eluted with water and 0.25 N HNO₃. The eluted Zn is titrated with standard EDTA (disodium salt) soln. Eriochrome black T is used as indicator and the end-point is determined spectrophotometrically. Small amounts of Mo, Pb, Pt, W, Cu, Fe^{III}, Mn, Ti, Th and Zr can be tolerated; Pb, Sn, In, Ti, Ga and U can be eliminated by chloroform extraction of the Zn as the pyridine thiocyanate from the eluates, the Zn being then withdrawn from the chloroform into an ammoniacal soln. and titrated. Pre-treatment of the resin and sample with methylarsonic acid greatly reduces the amount of Sn accompanying the Zn. For the determination of 5-mg and 0.5-mg amounts of Zn in mixtures containing 100 mg of total cations the results show no significant error. The standard deviations are ± 15 and ± 8 μ g, respectively. Results are given for a few alloys and a glass.

A. O. JONES

2658. Determination of zinc in copper alloys. B. Chew and G. Lindley (English Electric Co., Bradford, England). *Metallurgia, Manchr*, 1956, **53**, 45-47.—The chromatographic separation of Zn from copper alloys is carried out by dissolving 0.1 g of the sample in aqua regia, evaporating almost to dryness and re-dissolving in the solvent (96 parts of butanol and 4 parts of 20 per cent. v/v HCl). The soln. is then run through a moderately tightly packed 7-in. column of cellulose and the eluate is concentrated by evaporation to ≈ 10 to 20 ml and cooled; 50 ml of buffer solution (80 ml of aq. NH₃, sp. gr. 0.880, and 10 g of NH₄Cl per litre) are added, and the soln. is titrated with 0.1 N EDTA (disodium salt), with Eriochrome black T as indicator.

S. C. I. ABSTR.

2659. The reliability of methods for the determination of cadmium. A. Rokosz (Krakow Univ., Poland). *Roczn. Chem.*, 1955, **29** (4), 1119-1127.—The gravimetric determination of Cd as CdSO₄ involves a relative const. error of ± 0.12 per cent., due to tenaciously retained H₂SO₄ and H₂O; procedures proposed by various authors for abolishing this source of error are ineffective. The relative precision of this method is ± 0.19 per cent. The determination as CdS after drying at 120° C involves a relative constant error of ± 0.94 per cent., and the precision is about ± 1.2 per cent.; drying in a stream of H₂S abolishes the const. error, and the precision is then ± 0.54 per cent. Berg's gravimetric 8-hydroxyquinoline method (*Z. anal. Chem.*, 1927, **71**, 321) gives an absolute const. error of -0.3 mg, due to the solubility of the ppt., and has a precision of ± 0.7 mg; the volumetric (bromide-bromate) modification gives a const. error of -0.25 mg, and a precision of about ± 0.3 mg. Lange's volumetric 1:2-naphthaquinone method

(*Z. anorg. Chem.*, 1922, **122**, 332) involves a const. error, ascribed to difficulty in detecting the end-point, and has a precision of about ± 1 mg; Berg's modification (*Ber.*, 1927, **60**, 1664) gives no const. error, and has an absolute precision of ± 0.5 mg.

R. TRUSCOE

2660. Inorganic paper-chromatography. XXV. Separation and detection of zinc, beryllium and aluminium and its application to systematic analysis. Shirō Harasawa and Takashi Sakamoto (Faculty of Eng., Yamaguchi Univ., Ube). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 168-171.—Experiments were carried out with acetone, methanol, ethanol, propanol, butanol and pentanol, and their mixtures with mineral acids as developers. A satisfactory separation of Zn, Be and Al was effected when a mixture of HCl and aliphatic alcohols was used. The R_F values of Zn, Be and Al increase with increasing concn. of HCl, but they decrease in this sequence for all the developers used. The spots are detected with dithizone-CCl₄ soln. (Zn), alizarin red S (Al) and quinalizarin (Be).

K. SAITO

2661. Determination of metals with a standard solution of potassium ferrocyanide. VIII. Determination of cadmium. Yoshio Fujita (Faculty of Eng., Osaka Univ., Miyakojima-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 15-18.—In the volumetric determination of Cd, with K₄Fe(CN)₆ starch-iodine soln. is used as an indicator. The titration should be carried out slowly (5 to 10 sec. per drop) in a sulphate soln. (pH 6.0 to 6.6) for satisfactory results (error < 0.3 per cent.) to be obtained. Interference is caused by most metal ions except those of the alkalis, Al and Mg.

K. SAITO

2662. The photocolorimetric determination of cadmium in polymetallic ores by means of dithizone. D. P. Shcherbov and N. K. Shevtsova. *Izvest. Akad. Nauk Kazakh. SSR, Ser. Khim.*, 1955, (8), 105-113; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,507.—The determination of Cd is based on measurement of the intensity of the red colour of a soln. of the Cd-dithizone compound, separated from Bi, Fe, Mn, Pb and Zn by extraction with CCl₄ in alkaline medium in the presence of tartrate; Cu is removed by a preliminary extraction from acid soln. Decompose 0.1 g of the polymetallic ore (0.01 to 0.75 per cent. of Cd, ≥ 5 per cent. of Cu) with 10 ml of aqua regia and evaporate to dryness; add 5 ml of HCl (1:1) and evaporate once more. Moisten the dry residue with HCl (1:1), dissolve it by warming with 10 ml of water and make the vol. up to 50 ml. Acidify an aliquot with HCl, add 5 ml of 0.05 per cent. dithizone in CCl₄ and shake for 1 to 2 min. Separate the violet organic layer (dithizone-Cu compound). Extract the aq. soln. repeatedly until the violet colour changes to green. To the aq. layer add 2 ml of 20 per cent. K Na tartrate soln., a crystal of hydrazine sulphate, 15 ml of 10 per cent. NaOH and 10 ml of 0.01 per cent. dithizone in CCl₄. To the lower layer (containing the Cd-dithizone and some Zn-dithizone) add 5 ml of 5 per cent. NaOH soln. Wash the orange-red layer repeatedly with NaOH soln. until colourless. Wash the dithizone-Cd soln. with water and measure the extinction, with a green filter, at 500 to 520 μ . The colour of the soln. is stable for 6 hr. A blank determination is made with the reagents. Results are satisfactorily reproducible for < 15 μ g of Cd in 10 ml of soln.

C. D. KOPKIN

2663. Determination of traces of metals by the extraction of inorganic compounds with organic solvents. II. Micro-determination of mercury by use of its thiocyanate complex. Hidehiro Gotō and Shigerō Ikeda (Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 79-82.—The extraction of the thiocyanate complex of Hg^{II} was studied with ethyl acetate (I), isobutyl alcohol (II) and *n*-butanol and their binary mixtures. The absorption spectrum of the organic layer was examined with a Beckman spectrophotometer. When the complex is extracted with a mixture of I and II (3 + 1) from an aq. soln. of pH 3.5 to 6.5 the extinction coeff. at 285 μ is proportional to the amount of Hg (< 200 μ g in 5 ml). For Hg (< 100 μ g), complete extraction is achieved by use of one 5-ml portion. Other heavy-metal ions, such as Pb (> 50 μ g for 100 μ g of Hg), Co^{++} (> 5 μ g), Cu (> 50 μ g), Fe^{++} (> 10 μ g), Bi (> 50 μ g) and Cd (> 100 μ g), vitiate the estimation. K. SAITO

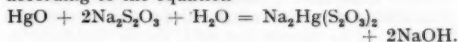
2664. Chemical analysis by the use of catalysed or induced reactions. VIII. Determination of mercury by an induced reaction with permanganate-oxalate. Shukichi Sakuraba (Dept. of Eng. Chem., Faculty of Eng., Shizuoka Univ., Oiwake, Hamamatsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 18-22.—Experimental conditions for the reduction of Hg with oxalic acid induced by KMnO_4 were studied for its application to the gravimetric analysis of Hg as Hg_2Cl_2 . The influence of pH, temp. and amounts of reagents was examined and a mechanism of the induced reaction is suggested. The sample (0.02 to 0.2 g of Hg) is introduced into a 0.1 *M* Na oxalate soln. (15 ml) containing KCl (10 per cent., 1 ml) and an amount of *N* HCl or H_2SO_4 sufficient to maintain a pH of 3.0 to 3.4. This mixture is kept on a water bath (50° to 60° C) and 0.1 *N* KMnO_4 (5 ml) is added. A sudden pptn. of Hg_2Cl_2 takes place. The soln. is set aside at room temp. for 40 to 60 min. and filtered through a sintered-glass filter; the ppt. is washed with acetone and weighed. Comparable amounts of other heavy metals, including Cu, Sn^{IV} , Sb, As^{III} , As^V , Bi and Pb, interfere.

IX. Determination of mercury by induced reduction with tervalent manganese-oxalate. Shukichi Sakuraba. *Ibid.*, 1956, **77** (1), 22-26.—A similar experiment was carried out with Mn^{III} in place of KMnO_4 . The mechanism by which the pptn. of Hg_2Cl_2 proceeds appears to be similar to that induced by KMnO_4 . The optimum pH range is 3.0 to 4.0. A gravimetric determination of Hg can be carried out similarly to that described above, but is slightly less accurate. K. SAITO

2665. Ascorbic acid as reducing agent in quantitative analysis. II. Estimation of mercuric chloride by reduction to mercurous chloride. G. Gopala Rao and U. Veereswara Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **150** (1), 29-39.—Quantitative reduction of HgCl_2 to Hg_2Cl_2 is possible with ascorbic acid (I) at pH 2.2 (redox potential < 0.26 V) without formation of metallic Hg. The rate of reduction increases with pH and with concn. of I. Interference by halide ions is severe. Procedure—Adjust the neutral soln. of HgCl_2 to pH 2.2 with citric acid - NaH_2PO_4 buffer (30 ml) and add a known excess of I (ratio of I to HgCl_2 < 5:1). Set aside for 40 min. to complete the reaction. Then add 20 per cent. KI (5 ml), H_2SO_4 (1:1) (5 ml, final concn. > 0.5 *N*), and 0.5

per cent. starch indicator (1 ml), dilute to 250 ml, and titrate with KIO_3 . Alternatively, after 40 min., collect the Hg_2Cl_2 , wash with a little cold water, dry at 100° to 110° C, and weigh. Thus 10 to 25 mg of HgCl_2 can be determined to within \pm 0.5 per cent.; the gravimetric results are slightly low owing to loss of Hg_2Cl_2 in the wash-water. J. P. STERN

2666. Alkalimetric method for the determination of mercuric chloride. A. B. Dutta (Pharm. Training Centre, Jalparguri, India). *J. Inst. Chem., India*, 1955, **27** (4), 282-284.—The method is based on the reaction of HgO with $\text{Na}_2\text{S}_2\text{O}_3$ to give a highly soluble complex sodium-mercury thiosulphate, with liberation of an equivalent amount of alkali, according to the equation—



Approx. 0.3 g of HgCl_2 is dissolved in 90 ml of water and \approx 2 ml of 20 per cent. NaOH are added dropwise until the HgO is completely pptd. The ppt. is washed three times by decantation and finally on a filter until free from alkali. The HgO is dissolved in a carefully neutralised solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 per cent. w/v) and the liberated alkali is titrated with 0.1 *N* HCl to methyl orange. The method is as accurate as the official B.P. method and can be used for the assay of sol. mercuric salts, but not in the presence of gold and silver salts, which also form complex salts with $\text{Na}_2\text{S}_2\text{O}_3$.

J. M. JACOBS

2667. Determination of metals with a standard solution of potassium ferrocyanide. VII. Determination of mercurous salt. Yoshio Fujita (Faculty of Eng., Osaka Univ., Miyakojima-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 12-15.—The volumetric determination of Hg^I (\approx 20 mg) with $\text{K}_3\text{Fe}(\text{CN})_6$ soln. was studied with K_2CrO_4 as an indicator. Satisfactory results (error < 0.3 per cent.) are obtained only when the titration is carried out slowly (2 to 10 sec. per drop) at a pH of 2.4 to 2.9. Metal ions, except those of Al, Mg, the alkaline earths and alkalis, interfere.

K. SAITO

2668. Determination of radium-A and radium-F in radioactive springs. Tomitaro Ishimori and Itsuhachiro Hatae (Faculty of Sci., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 122-124.—The method of extraction of polonium with dithizone (I) (*Ibid.*, 1950, **71**, 327) was applied to the determination of Ra-A and Ra-F in radioactive springs. The sample (mineral water containing CO_2) (200 ml) is acidified to produce a 3 per cent. HNO_3 soln. and vigorously shaken to remove radon and CO_2 . This soln. is extracted five times with I (200 mg per 100 ml of CCl_4) (a few ml each time) and the CCl_4 layers are combined and evaporated to dryness for subsequent measurement of Ra-F activity. For the determination of Ra-A, the same procedure is carried out rapidly (within 5 min.) (extraction with I only once) and the activity is plotted against the time (0 to 20 min.). Since the residual activity must be due to Ra-F (a part of the total Ra-F measured above), the Ra-A content in the sample water can be calculated by the use of the calibration factor obtained from the two data for Ra-F.

K. SAITO

2669. The spectral determination of boron in tourmaline. Yu. S. Plyshevskii. *Trudy Ural'sk. Nauch. Issledovatel. Khim. Inst.*, 1954, **2**, 280-283;

Ref. Zhur., *Khim.*, 1955, (19), Abstr. No. 43,266.—The samples are mixed with SiO_2 in the ratio 1:2, placed in a cavity in the angular electrode, and ignited in an a.c. arc discharge. The spectra are photographed on spectrograph ISP-22 on diapositive plates; current strength 10 amp., exposure time 2 min. (without preliminary ignition). The slit is illuminated without a condenser; for even illumination a frosted quartz plate is placed in front of the lens. Standards are prepared by mixing boric acid and SiO_2 to give a boron content of 0.5 to 8.0 per cent. The calibration curve has for co-ordinates $\Delta\epsilon$ and $\log C$. The analytical lines B 2497.03 Å and Si 2506.899 Å are used.

C. D. KOPKIN

2670. Colorimetric determination of small amounts of aluminum in chromium-nickel and magnesium alloys. V. I. Kuznetsov and R. B. Golubtsova. *Zavod. Lab.*, 1956, **22** (2), 161-162.—Methods based on the use of "arsenazo" are described. To determine Al in chromium-nickel alloys, the sulphate solution obtained after an initial attack on the sample (0.1 g) with HCl and HNO_3 , followed by evaporation with H_2SO_4 , is electrolysed with a mercury cathode, and the electrolyte is then evaporated and made up to 50 or 100 ml in a calibrated flask. An aliquot portion is treated with cupferron to remove Ti, Zr and Nb; the excess of reagent is removed from the filtrate by evaporation with H_2SO_4 and HNO_3 , and the solution is evaporated until H_2SO_4 is completely removed. The residue is dissolved in water, the solution is neutralised with aq. NH_3 and then made slightly acid with HCl; traces of Fe are reduced with ascorbic acid and the Al is determined colorimetrically with arsenazo. To determine Al in magnesium alloys, the solution of the sample (0.05 g) in HCl is diluted to 100 ml, and an aliquot portion, treated with cupferron if necessary to remove Ti or Zr, is reduced with ascorbic acid and then mixed with the reagent. G. S. SMITH

2671. Assay of basic aluminium acetate solution by titration with Complexone III. E. D. Aarnes and R. Klerstrand (Dept. Pharmacy, Oslo Univ., Norway). *Medd. Norsk Farm. Selsk.*, 1956, **18** (2), 17-23.—After a review of current official methods, a direct compleximetric titration of basic Al acetate soln. is described. *Procedure*—Dilute 1 g of basic Al acetate with water to a vol. of 25 to 30 ml, add 10 ml of acetate buffer (pH 5) and 10 drops of 0.5 per cent. alcoholic haematoxylin soln. Heat the faintly purple soln. to boiling point, when the colour of the soln. becomes deeper. Titrate at 80° to 100° C with a 0.1 M soln. of EDTA (disodium salt) till the colour changes to yellow. The results obtained are 1.5 to 2 per cent. lower than those obtained by the gravimetric oxine method, but are found to be consistent.

H. A. FISHER

2672. Microchemical determination of indium. J. Barlot (École Nat. Supérieure de Chimie, Toulouse, France). *Mikrochim. Acta*, 1956, (1-3), 179-183.—Most of the numerous reactions proposed for the microchemical crystalline identification of In have proved of little interest because of lack of specificity or sensitivity, especially when it is present with other metals of the same group. A modified procedure for the pptn. of rubidium or caesium chloro-indate is proposed; a sensitivity of 0.1 to 0.2 µg is claimed. Add one crystal of rubidium or caesium chloride to an HCl solution of In. Chloride

may be replaced by nitrate provided that the test solution contains a slight excess of HCl. Pptn. of metallic In by displacement with Zn, Al or Mg gives a precise indication under favourable conditions. Evidence of detection of In at the 0.1-µg level has been obtained. D. F. PHILLIPS

2673. Inorganic paper-chromatography. XXIV. Separation and detection of thallium, iron, titanium and zirconium and its application to systematic analysis. Shirô Harasawa and Takashi Sakamoto (Faculty of Eng., Yamaguchi Univ., Ube). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 165-168.—The paper chromatography of Tl (uni- and tri-valent), Fe^{III} , Ti and Zr was studied by the use of acetone, methanol and butanol, and their mixtures with mineral acids. Tervalent Tl was well developed with all developers used; Tl^I was well developed only with those containing HNO_3 and H_2SO_4 , remaining at the initial point in other cases. The R_F values for Ti and Zr are largely dependent on the water content in a mixture of acetone and HCl. For a systematic detection of these four elements, their hydroxides are dissolved in dil. HCl (1 + 1) and mixed with acetone (2.5 times the vol. of the HCl). The chromatogram obtained with this soln. provides R_F values of 1.0, 0.9, 0.4 and 0.2 for Tl^{III} , Fe^{III} , Zr and Ti, respectively, the spots being detected with KI, $\text{K}_4\text{Fe}(\text{CN})_6$ (for Fe^{III} and Ti) and alizarin red S. K. SAITO

2674. Compleximetric determination of rare earths. G. Brunisholz and R. Cahen (Univ. Lausanne). *Helv. Chim. Acta*, 1956, **39** (1), 324-325.—An accurate and rapid method for the titrimetric determination of rare-earth-metal ions by means of EDTA is given. The titration is carried out in a slightly acid solution, with a mixture of ammonium (or sodium) alizarinsulphonate and methylene blue as indicator. An accuracy within ± 0.5 per cent. is attained with La, Ce and Sm. C. A. FINCH

2675. Analytical studies of the fluorescence of samarium in calcium tungstate. C. G. Peattie and L. B. Rogers (Shell Development Co., Houston, Texas, U.S.A.). *Spectrochim. Acta*, 1956, **7** (6), 321-348.—A quantitative fluorimetric method has been developed based on initial formation of a slurry from calcium tungstate and a solution of tervalent samarium, followed by ignition at 400° C; the tungsten fluorescence may be used as internal standard if the Hg 2536-Å line is employed for excitation. Amounts of Sm as low as 2 µg per 1 g of CaWO_4 can be detected, although the range recommended is 60 to 3600 µg of Sm per 1 g at 20° C for the bands at 5630 Å, 5666 Å, 6417 Å, 6459 Å, 6507 Å and 6547 Å. The fluorescence of Sm is severely quenched by the presence of small quantities of other rare earths, e.g., neodymium and gadolinium in a sixfold excess completely wipe out the Sm bands, whilst a similar concentration ratio for europium reduces the Sm band by 30 to 40 per cent. D. G. HIGGS

2676. Liquid scintillation technique for measuring carbon-14 dioxide activity. J. M. Passmann, N. S. Radin and J. A. D. Cooper (Veterans Admin. Res. Hosp. & N.W. Univ. Med. School, Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 484-486.—A method is described for the determination of ^{14}C in large amounts of CO_2 with a liquid scintillation counter. The CO_2 need not be purified before counting and is dissolved in a toluene-methanol

medium by diffusion into a solution of high-mol.-wt. quaternary ammonium hydroxide. After being counted, the samples can be readily stored. The counting efficiency is independent of the amount of CO_2 , but does depend on the amount of amine, varying from 33 to > 67 per cent. The standard deviation of a set of nine similar samples of high activity was 0.34 per cent. of the mean value. The method may be useful for the determination of radioactive S by conversion into H_2S or SO_2 and then dissolving in a similar medium.

K. A. PROCTOR

2677. Titration of alkali cyanide with nickel sulphate solution. Tomoyuki Mukoyama (Faculty of Eng., Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1956, **5** (1), 12-16.—The use of murexide (I) for the titration of CN^- with Ni^{++} was studied with reference to interference of other anions, including halides, CO_3^{--} , acetate, SCN^- , NO_3^- , SO_4^{--} and PO_4^{--} . Alkali cyanide (≈ 0.3 g in ≈ 100 ml) is made basic with aq. NH_3 soln. (6 N, 8 ml) and titrated with 0.1 N NiSO_4 (error < 0.03 ml). Powdered I (0.03 to 0.05 g of I with 100 g of NaCl) is added before the titration. No appreciable interference results from CrO_4^{--} , $\text{Fe}(\text{CN})_6^{--}$ and the above-mentioned anions. Ferricyanide readily decomposes I. The presence of Cu, Zn, Co or Ag vitiates the estimation. The error is increased by CaCl_2 , but this effect is eliminated by the addition of a slight excess of oxalate.

K. SAITO

2678. Spectrophotometric micro-determination of silicon in cathode nickel. W. Gann (Telefunken G.m.b.H., Ulm, Germany). *Z. anal. Chem.*, 1956, **150** (4), 254-262.—Silicon (0.2 to 0.004 per cent.) "activator" in cathode nickel (5 to 50 mg) is determined spectrophotometrically as the molybdenum-blue complex (λ_{max} at 800 μ) with an accuracy within ± 5 per cent. Tungsten interferes. *Procedure*—Dissolve the Ni in HNO_3 (1:1) (1-25 ml) with warming, add sulphamic acid (10 per cent.) (1-25 ml), and adjust to pH 4. Dilute to 25 ml to make the stock soln. To 10 ml add H_2SO_4 (1:3) (0.25 ml exactly) and ammonium molybdate soln. (2.5 ml) (concn. not given). Set aside for 5 min. then add more H_2SO_4 (1:3) (7.5 ml). Shake, add fresh 1 per cent. SnCl_2 (0.6 ml), dilute to 25 ml, and determine the extinction (within 25 min.) at 800 μ against that of the stock soln. For very small amounts of Si (< 0.004 per cent.), a known amount of Si in the form of water-glass soln. is added to bring the total content of Si to ≈ 0.01 per cent.; this halves the accuracy.

J. P. STERN

2679. Spectrochemical analysis of silicon carbide. F. Rost (Inst. of Mineralogy, Tech. Hochschule, Munich, Germany). *Mikrochim. Acta*, 1956, (1-3), 343-352.—Spectrochemical analysis of silicon carbide offers many advantages over chemical methods. The fundamentals of spectrographic methods are discussed together with the difficulties of obtaining suitable calibration standards. The use of pure SiO_2 (quartz) as a base material for the preparation of synthetic comparison standards is studied by the preparation of emission intensity vs. time diagrams, and it is shown that the similarity in behaviour to SiC as well as the high purity ($\approx 10^{-4}$ per cent. of total impurities) makes it suitable for this purpose. Conditions for arc excitation are stated for the determination of Fe, Al, Ti and Mg, the lines used being Fe 3020.6, Al 3082.2, Ti II 3234.5 and Mg II 2802.7, each being compared with Si

2987.7. The mean error varies from 7 to 15 per cent. Properties of various samples of SiC indicate a definite dependence on the aluminium content, which can be influenced by extremely high or low values for Fe and Ti.

D. F. PHILLIPS

2680. Quantitative spectrochemical determination of trace elements in silicon carbide with the carbon arc. F. Hegemann, K. Giesen and C. von Sybel (Tech. Hochschule, Munich, Germany). *Ber. dtsch. keram. Ges.*, 1955, **32** (11), 329-333.—Full details are given of the use of a Zeiss Q24 quartz spectrograph, a Zeiss Rapid Photometer and a visual comparator. The sample was contained in the hollow anode of a 6.5-amp. arc. The purest commercial SiC (Fe 0.05, Al 0.032, Ti 0.008, Ca 0.015, Mg 0.01 per cent., determined spectrographically by the addition of known amounts of the same order) was used to prepare calibrating mixtures with the oxides containing 0.01 to 3 per cent. of Fe, Al, Ti, Zr, Ca and Mg. The internal and external standards were Si, and Ni and Sn, respectively, and the intensity comparisons were made on Fe 3020.6 and 3047.0 (above 0.1 per cent. of Fe), Al 3082.1, Ti 3088.0, Zn 3438.2, Ca 4226.7, Mg 2802.7, Cu 3274.0 and V 3185.4 Å. The ratio of sample to spectral carbon mixture was 1:2 and 1:1 for the photometric and visual comparison methods, respectively. The reproducibility of the photometric determination of Fe, Al, Ti and Zn was ± 3.6 per cent. and the values agreed well with those of a National Bureau of Standards sample of SiC. More rapid but less accurate measurements of the above elements and of Ca, Mg and traces of Cu and V were made with the visual comparator. Analytical data for 10 different samples of SiC are recorded.

J. A. SUGDEN

2681. An accelerated method for the determination of silica and magnesium oxide in dunite and in forsterite refractories. S. T. Balyuk and B. A. Fainerman. *Ogneupory*, 1955, **1**, 44-47; *Ref. Zhur. Khim.*, 1955, (19), Abstr. No. 43,289.—To determine SiO_2 , bake the weighed sample with Na_2CO_3 (950°C). Dissolve the baked mass in HCl (1:1), add H_2SO_4 (sp. gr. 1.84) and HCl (sp. gr. 1.19) and heat to fumes of SO_3 . Dilute with water, filter off the pptd. SiO_2 dry, ash, ignite and check the purity of the SiO_2 in the normal way. To determine MgO, bake the weighed sample as above, dissolve in HCl (1:1), add NH_4Cl and H_2O_2 soln. (3 per cent.). Remove Fe^{+++} and Al^{+++} with aq. NH_3 soln. in the presence of methyl red. Boil the filtrate, then cool and make up to a definite vol. Dilute an aliquot, add aq. NH_3 soln. and oxine soln. (1.5 per cent.), and heat on a water bath at 70°C. Filter off the pptd. $\text{Mg}(\text{C}_8\text{H}_7\text{ON})_2$. Wash the ppt., dissolve it in HCl (1:1), and titrate the soln. with excess of KBrO_3 -KBr soln. in the presence of methyl orange, and complete the titration iodometrically.

C. D. KOPKIN

2682. Use of acridine in the analysis of heteropoly acids. I. Gravimetric estimation of germanium as acridine molybdoorganate. P. R. Subbaraman (Nat. Chemical Lab. of India, Poona). *J. Sci. Ind. Res.*, B, 1955, **14** (12), 640-643.—A gravimetric method for estimating milligram amounts of Ge, based on the reaction in acid solution between molybdoorganate acid, $\text{H}_2\text{GeMo}_{12}\text{O}_{40}$, and acridine, is described. A sparingly soluble ppt. corresponding to the formula $(\text{C}_{13}\text{H}_9\text{N})_2\text{Ge}(\text{Mo}_3\text{O}_{10})_4$ is obtained. The method compares favourably with the recognised oxine molybdoorganate

method and has the advantage that no empirical factor is used. Sulphate, perchlorate, chloride, oxalate, tartrate and citrate, when present in appreciable amounts, interfere, as do P, Si, As, W and V. I. JONES

2683. The effect of silicic acid on the determination of a small amount of germanium. Hiroshi Nishida (Ind. Training Inst. of Iwate Prefecture, Uchimaru, Morioka). *Japan Analyst*, 1956, **5** (1), 17-20.—A significant amount of germanium is adsorbed on the surface of amorphous silica produced by the decomposition of silicates with HNO_3 or H_2SO_4 . The distillation of GeCl_4 is also incomplete in the presence of silica. The extent of interference depends on experimental conditions, but appears to increase with the increasing surface area of silica. It is suggested that removal of SiO_2 with HF and H_2SO_4 is necessary for an accurate estimation. K. SAITO

2684. The influence of certain elements on the intensity of the spectral lines of tin. V. Engel'slit. *Sbornik. Nauch. Rabot Stud. Kirghiz Univ.*, 1954, (1), 11-16; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,479.—The influence of compounds of K, Na, Ba, Sc, Sr, Al, Ca, Zn, Cd and Hg on the intensity of the following Sn lines—2483.0, 2840.0, 2850.6, 2863.3, 3032.8, 3034.1, 3175.0 and 3262.3 Å—was studied. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ being used. Photographs were taken with spectrograph ISP-22, and a slit width of 5 μ . Excitation was by a 5-amp. a.c. arc; the distance between the angular electrodes was 3 mm. The SnCl_2 and compound being studied were mixed in a cavity in the electrode. The lines were measured photographically on microphotometer MF-2. The greatest increase in intensity of the Sn lines was effected by the addition of KCl. The ionisation potential of K is lower than that of many substances, therefore the presence in the arc of a significant amount of K overrides the influence of other mixtures on the temperature of the arc. It is recommended that standards be prepared from the bases being studied. C. D. KOPKIN

2685. Determination of tin in bismuth. I. Levitan (Weizmann Inst. Sci. Rehovoth, Israel). *Spectrochim. Acta*, 1956, **7** (6), 395-396.—Details are given for the spectrographic determination of small amounts (0.01 to 1 per cent.) of tin in bismuth. Under the conditions described, the lines Sn 3034.12 Å and Bi 3034.87 Å were found to be of equal intensity for an alloy containing 0.14 per cent. of Sn. Analysis may be carried out on as little as 0.02 g. D. G. HIGGS

2686. The electrolytic determination of lead by cathodic precipitation. N. D. Podobed. *Soobshch. Nauch. Rabotakh. Chlenov. Vsesoyuz. Khim.*, 1954, (3), 35-37; *Ref. Zhur., Khim.*, 1955, (15), Abstr. No. 31,886.—The method of determining Pb by cathodic pptn. as metal is modified by reducing the quantity of sample, increasing the current, and using mechanical stirring. *Procedure*—Dissolve the sample of metallic Pb (5 to 200 mg), and to the neutral soln. add 4 ml of HNO_3 (sp. gr. 1.14), 2 to 6 g of gallic acid as depolariser and 5 to 10 ml of ethanol and dilute to 250 ml. Warm the soln. to between 75° and 80° C and electrolyse for 15 to 60 min. with a platinum-foil electrode, previously coated with Cu, at 4 to 4.5 amp. with mechanical stirring. For a sample ≥ 0.1 g, electrolyse for 20 min. The Pb separates almost completely, the ppt. being satisfactorily dense, pale grey and finely crystalline. The described method is recommended

for the analysis of food products and biological specimens. Copper and other heavy metals interfere. C. D. KOPKIN

2687. An amperometric method for determining titanium. V. M. Peshkova and Z. A. Gallai. *Vestnik. Moskov. Univ.*, 1954, (10), 73-81; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,510.—The Ti^{+++} soln. in $\text{N H}_2\text{SO}_4$ (which may contain Al, Ni, Zn and Cr) is titrated with 0.1 M soln. of cupferron at a potential of -0.65 to -0.70 V with respect to the saturated cadmium electrode. Only the cupferron is reduced; 0.5 to 5 mg of Ti^{+++} are titrated in 15 to 20 ml of $\text{N H}_2\text{SO}_4$. The composition of the ppt. is $\text{Ti}(\text{C}_6\text{H}_5\text{NO})_4$. If Fe, V, Zn, Cu, Nb or Ta is present, the Ti is extracted first. To determine Ti in the presence of Fe, an oxidimetric method of amperometric titration of Ti^{+++} by FeCl_3 soln. at a potential of -0.35 to -0.04 V with a rotating platinum electrode (500 r.p.m.) has been evolved. To increase the stability of Ti^{+++} with respect to atmospheric oxygen, $(\text{NH}_4)_2\text{SO}_4$ is introduced into the soln. being titrated. Usually the Ti^{+++} soln. being titrated is added to a definite vol. of a mixture (10:1) of H_2SO_4 and saturated $(\text{NH}_4)_2\text{SO}_4$ soln. Up to the equivalence point the current remains constant, then increases proportionally to the excess of FeCl_3 . If the soln. to be analysed contains $\text{Ti}(\text{SO}_4)_2$, $(\text{NH}_4)_2\text{SO}_4$ is added; then Ti^{+++} are reduced to Ti^{++} by passage through a cadmium reductor. The Ti^{+++} are measured by amperometric titration with FeCl_3 soln. Considerable quantities of Fe, Al and Ni do not interfere. Large quantities of Cr render the titration more difficult, but the determination of Ti in chrome-nickel steels of type 18-8 can be carried out with a relative error of ≈ 2 per cent. In the absence of substances oxidised by NH_4VO_3 or $\text{K}_2\text{Cr}_2\text{O}_7$, these reagents may be used for the oxidimetric determination of Ti^{+++} with the rotating platinum electrode at a potential of +0.5 V. C. D. KOPKIN

2688. A new highly selective method for detecting zirconium with catechol violet and Complexone [III]. H. Flaschka and F. Sadek (Nat. Res. Council, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 1956, **150** (5), 339-345.—Small amounts (e.g., one drop of 10^{-4} M soln.) of Zr give a deep-blue complex with catechol violet in the presence of EDTA at a pH of 4 to 6.5. Most interfering ions are masked by the EDTA, but Sb^{III} and Sn^{IV} must be removed by use of aq. NH_3 ; complex-forming anions, such as oxalate, tartrate, citrate and fluoride, also interfere. A. R. ROGERS

2689. Spectrophotometric determination of zirconium in thorium. L. Silverman and D. W. Hawley (Atoms International, Canoga Park, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 806-808.—For the determination of Zr (0.005 to 0.35 per cent.) in 200-mg samples of Th, an excess of alizarin red S is used to form a lake, the extinction of which is measured at 540 m μ . Acetone and heat are used to develop and stabilise the colour for 3 hr. By carrying out the colour development at a high controlled acidity, any interference from metals normally present in Th (except Hf) can be avoided. The standard curve is linear for 0.05 to 0.7 mg of Zr. The conditions of colour development, reagent concn., acidity, and concn. of Th and Zr must be rigidly controlled for reproducible results. The reproducibility is about 0.01 per cent., with a standard deviation of 0.002 per cent. K. A. PROCTOR

2690. Determination of small quantities of hafnium in zirconium by X-ray spectroscopy. J. Despujols and D. Lumbroso (Phys. Chem. Lab., Fac. Sci., Paris). *J. Chim. Phys.*, 1956, **53**, 108-110.—By measuring the intensity of the L_{β_2} radiation from Hf with a spectrometer of the curved-crystal type and a Geiger counter, it has been found possible to determine several hundredths of 1 per cent. of Hf with an absolute error of the order of 1.5×10^{-4} . S. C. I. ABSTR.

2691. Use of catecholsulphonaphthalein in colorimetric analysis. II. Photometric determination of thorium. M. Svach (Inst. Anal. Chem., Montan-hochschule, Ostrau, Czechoslovakia). *Z. anal. Chem.*, 1956, **149** (6), 414-416.—Catecholsulphonaphthalein (catechol violet) (I) forms a red complex with Th in acidic soln. which permits its photometric determination. The Beer-Lambert law is obeyed for 100 to 600 μg of Th in 25 ml of soln. Complexing anions, Fe^{III} (red complex with I) and Bi (blue complex with I) interfere. Procedure—Add to the soln. of Th (100 μg per ml) a drop of 0.1 per cent. aq. I, and dilute to 25 ml with acetic acid-Na acetate buffer (pH 3-6). Determine the extinction at the absorption max. (480 $m\mu$) after 20 min. J. P. STERN

2692. Thoron-tartaric acid systems for spectrophotometric determination of thorium. F. S. Grimaldi and M. H. Fletcher (U.S. Geological Survey, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 812-816.—The use of tartaric acid as a masking agent for Zr in the spectrophotometric determination of Th with thoron is described. meso-Tartaric acid was found to be the most effective agent. A dilution method for the direct determination of Th in monazite concentrates is given.

K. A. PROCTOR

2693. Analytical aspects of some azo dyes derived from chromotropic acid. IV. Spectrophotometric determination of thorium with 1:8-dihydroxy-2:7-di-(4-sulphonaphthylazo)naphthalene-3:6-disulphonic acid. S. K. Datta (Gov. Coll., Darjeeling, India). *Z. anal. Chem.*, 1956, **150** (5), 347-355.—Thorium reacts with the dye 1:8-dihydroxy-2:7-di-(4-sulphonaphthylazo)naphthalene-3:6-disulphonic acid (I) to form a water-soluble blue-violet I:Th (2:1) complex, which shows maximum absorption at 640 $m\mu$ and can be used for the spectrophotometric determination of Th. Results are accurate to within ± 10 per cent. The absorption is greatest at pH 3 and is stable for 24 hr. Beer's law is obeyed in the concn. range 0 to 4 p.p.m. of Th; the practical limit of sensitivity is about 0.05 p.p.m. Estimation is possible in the presence of many ions, but Fe^{+} , Fe^{++} , Zr^{+++} , Au^{+++} , Cu^{++} , Ni^{++} , PO_4^{+++} and F^{-} interfere. Procedure—Add a 0.1 per cent. soln. of I (0.6 ml) to the sample soln. (containing ≈ 0.1 mg of Th). Adjust the pH to 3 with 0.01 N HCl, and dilute to 25 ml. Measure the extinction at 640 $m\mu$ against a reagent blank and calculate by the use of a calibration curve. A. R. ROGERS

2694. 5:7-Dibromo-oxinates of thorium—a spectrophotometric study. K. V. S. Rama Rao and B. S. V. Rhagava Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **150** (1), 21-24.—The complexes of Th with 4 and 5 mol. of 5:7-dibromo-8-hydroxyquinoline (I) differ in u.v. absorption (curves are given for soln. in dioxan, acetone and CCl_4). Neither I nor the complexes obey Beer's law exactly, but conditions suitable

for the colorimetric estimation (at 390 $m\mu$) of Th may be selected within narrow limits of concn. Thus for 0.15 and 0.35 mg of Th the accuracy is within ± 3 per cent. J. P. STERN

2695. A study of the reaction between thorium and 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (thoron). L. P. Adamovich and V. M. Rutman. *Uch. Zap. Khar'kov. Univ.*, 1954, **54**; *Trudy Khim. Fak. i Nauch. Issledovatel. Inst. Khim.*, **12**, 203-208; *Ref. Zhur.*, *Khim.*, 1955, (15), Abstr. No. 31,881.—A study of the composition of the compound formed by the interaction of Th with 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (I) by Ostromyslenskii's method has shown that the components react in the ratio 1:2, the ions reacting being Th^{+++} and a bivalent anion obtained by acidic dissociation of I. The optimum pH is 1.65. The constant of complex formation is $(7.9 \pm 0.9) \times 10^9$. C. D. KOPKIN

2696. Improved conditions for the sodium phenoxide-sodium hypochlorite method for the determination of ammonia. A. B. Crowther and R. S. Large (Dept. of Atomic Energy (I.G.), Springfield Works, Salwick, nr. Preston, Lancs., England). *Analyst*, 1956, **81**, 64-65.—An examination of the method of Riley (cf. *Anal. Abstr.*, 1954, **1**, 825) for the determination of NH_3 in water showed that (i) by storing separate soln. of sodium phenoxide and NaOH and mixing as required, a more constant reagent is obtained; (ii) with the use of industrial methylated spirit to dissolve the phenol the sensitivity is improved; (iii) when acetone is included in the industrial spirit the blue colour develops rapidly and reaches its max. intensity in 20 min., and (iv) with these modifications addition of MnSO_4 can be omitted. The phenol (62.5 g) is dissolved in industrial spirit, 18.5 ml of acetone are added and the vol. is adjusted to 100 ml with industrial spirit. This soln. (20 ml) is mixed with 20 ml of 27 per cent. w/v aq. NaOH soln. and diluted to 100 ml. This reagent (4 ml) is added to the test soln. diluted to 10 ml with water; 3 ml of NaOCl soln. (0.9 per cent. of available Cl) are added and the mixture is diluted to 25 ml with water. After 20 min. the extinction is measured in a Spekker absorptiometer, with a Calorex H503 heat filter and an Ilford No. 607 filter and a 2-cm cell. Graphs are linear up to at least 80 μg of N for a vol. of 25 ml and a 1-cm cell, and up to 200 μg for a vol. of 50 ml and a 1-cm cell.

A. O. JONES

2697. The determination of nitrate ion in solutions containing nitrites. II. N. P. Komar' and I. V. Martynchenko. *Uch. Zap. Khar'kov. Univ.*, 1954, **54**; *Trudy Khim. Fak. i Nauch. Issledovatel. Inst. Khim.*, **12**, 253-262; *Ref. Zhur.*, *Khim.*, 1955, (15), Abstr. No. 31,905.—It is established that the reagents recommended for the removal of NO_2^{-} before subsequent determination of NO_3^{-} are unsuitable, because they all simultaneously decompose NO_3^{-} . A new method has been evolved for the removal of NO_2^{-} with the o-aminoanilide of diphenic acid (I) (Krasovitskii and Kocherginaya, *Dokl. Akad. Nauk SSSR*, 1952, **86**, 1121). The interaction of I with other ions is studied; the suitability of I for the removal of NO_2^{-} before qual. detection of NO_3^{-} is demonstrated.

C. D. KOPKIN

2698. New methods for the analysis of nitrous gases. K. Peters and H. Strachil (Inst. für Verfahrenstechnik u. Technol. Brennstoff. Tech.

Hochsch., Vienna). *Angew. Chem.*, 1956, **68** (8), 291-295.—Methods are described for the determination of "combined N" and "degree of oxidation" of nitrogen oxides in the presence of O, based on the use of solid absorbents. For combined N, AgMnO_4 or NaClO_2 is used; the N is then determined by Devarda's method. For degree of oxidation, Na_2CO_3 is used as primary absorbent to give a differential assay, according to the equations $2\text{NaOH} + \text{N}_2\text{O}_3 = 2\text{NaNO}_2 + \text{H}_2\text{O}$; and $2\text{NaOH} + 2\text{NO}_2 = \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O}$; titration with permanganate gives the content of NaNO_2 and Devarda's method the total N. The oxide NO is not absorbed by the Na_2CO_3 and must be determined separately ("secondary absorption"). Details are given for the calculation of combined N and degree of oxidation from the titration data. The methods are claimed to be more accurate and rapid than earlier processes. A. R. ROGERS

2699. Colorimetric micro-determination of phosphorus. J. Carles (Lab. de Physiol. Végétale, Inst. Catholique de Toulouse). *Bull. Soc. Chim. Biol.*, 1956, **38** (1), 255-257.—An adaptation of a U.S. official method of determining phosphoric acid in fruit is described for application to chromatograms. *Procedure*—Spots from a paper chromatogram containing P are ashed at 560° to 570°C and the residue is heated to fumes with HClO_4 and taken up in water. The solution (4 ml containing $< 10\text{ }\mu\text{g}$ of P) is acidified with 1 ml of 3 N H_2SO_4 , then made alkaline with 1 ml of 3.6 N NaOH and just acidified to Na alizarinsulphonate with N H_2SO_4 . The tube containing the solution is heated on a boiling-water bath for 5 min. and 1 ml of a molybdenum-blue reagent, prepared by diluting a stock reagent of molybdenum blue (0.11 N to permanganate) in H_2SO_4 with water, is added. After a further 20 min. on the water bath, the tube is cooled, the contents are made up to 10 ml and the extinction is determined (650 to 700 $\text{m}\mu$) against a blank. The method permits about 20 determinations per hour with a precision of $\approx \pm 0.1\text{ }\mu\text{g}$. E. J. H. BIRCH

2700. Rapid volumetric determination of hypophosphites. D. Kőszegi and É. Salgó (Univ. Szeged, Hungary). *Z. anal. Chem.*, 1956, **150** (4), 262-267.—The method for determining H_2PO_2^- by oxidation with an excess of neutral KMnO_4 (Kőszegi, *Ibid.*, 1926, **68**, 216) has been simplified and now takes ≈ 20 min.; 10 to 50 mg of $\text{Ca}(\text{H}_2\text{PO}_2)_2$ or KH_2PO_2 are determined with an accuracy within ± 0.2 per cent. *Procedure*—Add 40.0 ml (from a burette) of 0.1 N KMnO_4 to the neutral soln. of H_2PO_2^- (0.2 per cent.) (20 ml) and boil gently for 5 min. Cool the mixture, add KI (1 g) and dil. HCl (20 ml, to dissolve the MnO_2), and titrate the I liberated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (starch indicator). J. P. STERN

2701. Dichromatic estimation of phosphite and hypophosphite. Silver salt catalysis. G. Gopala Rao and K. Bhaskara Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **150** (5), 333-339.—Phosphites and hypophosphites can be determined quant. by heating with excess of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the presence of a Ag^+ catalyst, and back-titrating with Fe^{++} soln. *Procedure*—To the sample (10 ml, $\approx 0.01\text{ M}$ in phosphite or hypophosphite) add 0.05 N $\text{K}_2\text{Cr}_2\text{O}_7$ (20 ml) and 5 per cent. Ag_2SO_4 soln. (2 ml) and dilute to 50 ml, adding enough H_2SO_4 to make the final concn. 2 M. Heat on a bath of boiling water for 60 min., cool and titrate with standard ferrous ammonium sulphate soln. A. R. ROGERS

2702. Oxalate method of determining phosphoric anhydride in apatite concentrates and apatite-nepheline ores. L. D. Nikitina ("Apatit" Combine). *Zavod. Lab.*, 1956, **22** (2), 154-157.—Calcium, together with any strontium and traces of rare earths, is pptd. as oxalate with a known vol. of 0.20 to 0.23 N oxalic acid from a neutralised chloride solution of the apatite concentrate; the oxalate is filtered off, and the excess of oxalic acid in the filtrate is determined by titration with permanganate. Because of the constancy of the ratio of phosphate to alkaline earths in apatites, the results obtained may be used to calculate the phosphate content. G. S. SMITH

2703. Separation of bismuth with arsanilic acid. R. Pietsch (Inst. for Inorg. and Anal. Chem., Univ. Graz, Austria). *Z. anal. Chem.*, 1956, **150** (3), 190-192.—By the use of arsanilic acid, Bi can be pptd. quant. in the presence of Co, Ni, Cu, Zn, Pb, Ag, Cd, Al, Mg and the alkaline-earth metals. Arsenic must be present as As^{III} and must not exceed eight times the amount of Bi. The method is not valid in the presence of Hg^{II} , Fe^{III} , AsO_4^{--} , MoO_4^{--} and WO_4^{--} . The excess of arsanilic acid in the filtrate after the pptn. of Bi does not interfere with compleximetric titrations nor with many gravimetric separations of the remaining metals. J. H. WATON

2704. The analytical application of -onium compounds. VII. Polarographic behaviour of tetraphenylphosphonium chloride towards bismuth. Mutsuaki Shinagawa, Hiroshi Matsuo and Hiroyuki Nezu (Chem. Dept., Faculty of Sci., Hiroshima Univ., Higashisenda-machi, Hiroshima). *Japan Analyst.*, 1956, **5** (1), 20-23.—Tetraphenylphosphonium chloride (I) was synthesised (*cf.* Dodorow *et al.*, *Ber.*, 1928, **61**, 207; Willard *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 737) and its polarographic behaviour studied. The wave shows a max. at -1.85 V vs. the S.C.E. and the height is proportional to the concn. for 1.0×10^{-2} to $5.0 \times 10^{-5}\text{ M}$ soln. in 0.1 M KCl. No appreciable change in the shape of the wave and in the $E_{\frac{1}{2}}$ was observed with change in pH. I produces ppt. with heavy metals, including Hg, Cu, Cd, Sn^{++} , Sn^{+++} , Sb and Co, and gives a ppt. with Bi in a molar ratio 1:1. The amperometric titration of Bi^{+++} can be effected (at -0.7 V) in a neutral soln. of KI with an error < 1 per cent. K. SAITO

2705. Photometric determination of microgram quantities of vanadium in brine and common salt with diphenylaminesulphonate. Shizo Hirano, Hitoko Murayama and Mitsuko Kitahara (Inst. of Techno-Anal. Chem., Faculty of Eng., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst.*, 1956, **5** (1), 7-11.—A micro amount of V ($< 100\text{ }\mu\text{g}$ per litre) in NaCl soln. (which causes a marked lowering of current efficiency during electrolysis) is co-pptd. with $\text{Fe}(\text{OH})_3$ and photometrically determined with Na diphenylaminesulphonate (I). The sample (100 to 500 ml) is treated with HCl (1 + 2) to produce a $\approx 0.5\text{ N}$ HCl soln. and heated to remove Cl. In the presence of Hg ($> 0.5\text{ mg}$), H_2S is passed through, the pptd. HgS being filtered off. The filtrate is boiled, treated with NH_4Cl (5 g), $\text{Fe}_2(\text{SO}_4)_3$ (0.5 per cent. of Fe, 10 ml), H_2O_2 (30 per cent., 10 drops) and aq. NH_3 soln. to ppt. $\text{Fe}(\text{OH})_3$, which adsorbs all the V. The ppt. is filtered off and dissolved in warm H_2SO_4 (1 + 3, 20 ml), then transferred to a measuring flask with H_2SO_4 (1 + 1, 30 ml) and H_3PO_4 (15 ml). To the

soln. are added $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ (0.1 N, 1 ml) (to reduce higher oxides of V or Cr), urea (20 per cent., 5 ml) and a few drops of KMnO_4 (3 per cent.) until a purple colour persists for 1 min. The soln. is shaken with a few drops of NaNO_2 (3 per cent.) until the generation of nitrogen ceases. An aq. soln. of **I** (0.01 per cent., 5 ml) is added and the volume is made up to 100 ml. The extinction is measured at 570 m μ , then one drop of 0.1 N $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ is added to the cell (to decolorise the purple colour due to V) and the extinction is measured again; the amount of V is calculated from the difference. The blank is similarly measured, with the same amounts of reagents. Solid NaCl (50 to 100 g) is boiled with HCl (1 + 2, 300 ml) to produce a sample soln. For electrolytic slime, 5 to 10 g are dissolved in dil. HCl (50 ml) and filtered, and the $\text{Fe}(\text{OH})_3$ is pptd. The removal of Hg is carried out as above. For the removal of Ca, re-pptn. of $\text{Fe}(\text{OH})_3$ is necessary. The error is $\pm 3 \mu\text{g}$. The time taken for an estimation is < 40 min. K. SAITO

2706. Determination of vanadium in highly alloyed steels. Methods of Analysis Committee of B.I.S.R.A. (British Iron and Steel Res. Ass., 11 Park Lane, London). *J. Iron St. Inst.*, 1956, **182**, 156-159.—The procedure described in B.S. 1121: Part 27:1952 is used, but H_3PO_4 is omitted from the solvent mixture. It is recommended that the pre-oxidised form of diphenylamine indicator should be used at the reduction end-point with 0.025 N FeSO_4 . The use of F' is suitable for complexing any W present and excess of F' improves end-point detection. S. C. I. ABSTR.

2707. An electrometric method for determining sulphate ion. N. G. Cassidy (Dept. of Agric., Suva, Fiji Islands). *Analyst*, 1956, **81**, 169-175.—In the method described, the SO_4^{2-} are pptd. by $\text{Pb}(\text{NO}_3)_2$ in an alcoholic medium and the excess of Pb is determined by electrometric titration with 0.02 N K_2CrO_4 ; the end-point, a hydrolytic change, is at pH 5.5. Preliminary removal of PO_4^{3-} by FeCl_3 is necessary. Soluble silica does not interfere, but insol. forms do, probably by adsorption of Pb; Fe and Al would interfere but are removed in the initial pH adjustment and filtration. A response is obtained to < 0.001 milli-equiv. of SO_4^{2-} . A. O. JONES

2708. Bivalent tin - phosphoric acid: a new reagent for the determination of sulphate by reduction to hydrogen sulphide. Toshiyasu Kiba, Tomoo Takagi, Yooko Yoshimura and Ikuko Kishi (Kanazawa Univ.). *Bull. Chem. Soc. Japan*, 1955, **28** (9), 641-644.—The reagent is prepared by mixing SnCl_2 with dehydrated H_3PO_4 and boiling to expel HCl completely. The sample solution containing 5 to 20 mg of SO_4^{2-} is mixed with 6 to 10 ml of reagent in a tube connected to two flasks containing Zn acetate - acetic acid solution. A stream of CO_2 is passed rapidly through the apparatus and the mixture is then heated to 300°C, the evolved H_2S being absorbed in the flasks. An excess (normally 20 ml) of 0.02 N **I** solution is added to the flask contents and excess of **I** is back-titrated with 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$. S. C. I. ABSTR.

2709. The rapid volumetric determination of sulphate ions. E. Bakács and L. Szekecs (Univ. Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1956, **62** (4), 135-139.—The sample, containing ≈ 0.05 g of SO_4^{2-} , is dissolved in H_2O (3 to 5 ml). In the

presence of Cd^{2+} or Mn^{2+} , 0.1 N Na_2CO_3 is added to ppt. the hydroxides and until the colour is permanently pink to phenolphthalein. The pptn. is carried out at room temp. if Cd^{2+} are present, and in a hot soln. in the presence of Mn^{2+} . If Zn^{2+} , Al^{3+} , Bi^{3+} , Sn^{4+} or Sb^{5+} are present, 2 N NaOH soln. is added dropwise to ppt. the hydroxides and until the red colour to phenolphthalein becomes permanent. Acetic acid (0.01 N) is added to remove this colour, followed by sufficient ethanol to give a 30 per cent. soln. From a burette, 0.1 M Na_2CO_3 is added, in a vol. approx. equiv. to the SO_4^{2-} content, or in excess; the soln. is then titrated with 0.1 M BaCl_2 until the red colour disappears. A blank is carried out by using the same volumes of reagents as above. The accuracy depends on many factors; in the examples quoted, it was within ± 2 per cent. A. G. PETO

2710. Quantitative methods of analysis of compounds containing tellurium. J. Lautard and L. Pateau (Lab. de la Div. R.P.C. du C.N.E.T.). *Chim. Anal.*, 1956, **38** (5), 158-160.—Suitable methods of analysis are described for small samples of compounds containing Te having the following qual. composition: Te - Pb; Te - Bi; Te - Cd; and Te - Se - S - Cu - Ag. K. A. PROCTOR

2711. The determination of small quantities of chromium in soils and plants by spectral analysis. Yu. I. Belyayev and L. I. Pavlenko. *Trudy Biogekhim. Lab., Inst. Geokhim. i Anal. Khim., Akad. Nauk SSSR*, 1954, (10), 60-63; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,525.—In the determination of Cr in soils, quartz spectrograph Qu-24 was used, with a three-lens condenser in a d.c. arc. The electrodes were spectrally pure carbon, the sample cavity was 4 mm, and the width of the spectrograph slit was 0.015 mm. The sample of soil (20 mg) is ignited for 3-5 min. at 8 amp. The spectra of sample and standards are photographed on one plate (spectral plates, type III). The calibration curve is a straight line within the limits 0.035 to 0.085 per cent. of Cr; the analytical line is Cr 2677-159 Å; the error of the analysis is ± 16 per cent. In the analysis of plants, the sample (20 to 30 g) is dried at 150°C, ashed, and ignited at $< 500^\circ\text{C}$. The sample is ignited in the cavity in the angular electrode for 2-5 min. with an 8-amp. d.c. arc. The analytical line is Cr 4254-34 Å. The error is ± 15 per cent. C. D. KOPKIN

2712. Chelatometry. VIII. Decomposition product of Bindschedler's green as redox indicator. 3. Compleximetric estimation of tervalent chromium salts. P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1956, **150** (3), 186-190.—The Cr^{III} soln. is boiled with an excess of EDTA at a pH of 3.5, and the unchanged reagent is back-titrated with 0.1 M Fe^{III} soln., with the decomposition product of Bindschedler's green as redox indicator. *Procedure*—To 100 ml of a weakly acid Cr^{III} soln. are added 10 ml of chloroacetic acid - Na acetate buffer soln. and enough 0.1 M EDTA (disodium salt) to give an excess of < 5 ml. The soln. is boiled for 1 to 2 min. and then cooled to between 20° and 30°C. After the addition of 80 mg of indicator, the excess of EDTA is titrated with 0.1 M Fe^{III} soln. to the beginning of the colour change from red - violet to dark blue - violet. An indicator correction is made by deducting 0.04 ml of Fe soln. The method is modified to enable the simultaneous determination

of Fe^{III} and Cr^{III} to be effected. To a weakly acid soln. of Fe^{III} and Cr^{III} are added 10 ml of buffer soln. and 80 mg of indicator. The Fe^{III} is titrated with 0.1 *M* EDTA soln. to a bright-red end-point. An excess of EDTA is added and the soln. is boiled, cooled, and titrated with Fe^{III} soln. as described above. The preparation of the buffer soln. and indicator is described in an earlier communication (*Anal. Abstr.*, 1956, 3, 2088). For the estimation of Cr alone, it is recommended that ≈ 20 mg of Cr be used, and for the simultaneous estimation of Fe and Cr, from 10 to 50 g of Fe and up to 10 mg of Cr.

J. H. WATON

2713. A new colour reaction of molybdenum. P. M. Isakov. *Nauch. Byull. Leningrad. Gosudarst. Univ.*, 1955, (33), 31-35; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,526.—When salts of Mo are ground with $\text{Na}_2\text{S}_2\text{O}_3$ and KHSO_4 , a red-brown product is formed, which is probably a mixture of molybdenum sulphide and sulphur. For the detection of Mo in molybdenite, the mineral is first baked with free access to O. The possibilities of the use of the described reaction for the qual. detection of $\text{S}_2\text{O}_4^{2-}$, SCN^- and free S are indicated.

C. D. KOPKIN

2714. The photocolorimetric determination of molybdenum with phenylhydrazine. V. N. Tolmachev and V. G. Ostroverkhov. *Uch. Zap. Kharkov. Univ.*, 1954, 54; *Trudy Nauch. Issledovatel. Inst. Khim., Kh.G.U.*, (12), 269-271; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,251.—The applicability of the method for the analysis of different types of steel is indicated. Prepare standards from a soln. of $(\text{NH}_4)_2\text{MoO}_4$. To 10 ml of the soln. obtained add 3.5 to 6 ml of H_2SO_4 (sp. gr. 1.41) and 6 to 8 ml of phenylhydrazine (I) (0.09 g per ml). Boil the mixtures for 1 min., cool and dilute to 100 ml. Measure the extinction with the Vendt photocolorimeter (*Zhur. Obshch. Khim.*, 1937, 18, 2423). A blank is carried out at the same time. The concn. of Mo in the soln. must be within 1 to 7 μg per ml. Dissolve the steel samples by heating with 40 ml of H_2SO_4 [19 ml of H_2SO_4 (sp. gr. 1.41) plus 21 ml of H_2O]; in some cases conc. HNO_3 must be added. Evaporate the soln. to a smaller vol., add 70 ml of 20 per cent. alkali, cool, dilute to 200 ml and filter after 30 min. Neutralise 10 to 20 ml of filtrate with H_2SO_4 (sp. gr. 1.41) (25 to 30 ml) and evaporate to 10 ml. The standardisation of all processes (particularly the heating) and complete removal of HNO_3 promotes reproducibility and accuracy of results.

C. D. KOPKIN

2715. Determination of traces of metals by the extraction of inorganic compounds with organic solvents. III. Micro-determination of molybdenum by use of its thiocyanate complex. Hidehiro Gotô and Shigerô Ikeda (Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, 77 (1), 82-86.—The extraction of the thiocyanate complex of Mo^{V} , produced by the reaction of KSCN and a reducing agent (SnCl_2 or hydrazine sulphate) with Mo^{VI} , was studied with organic solvents, including amyl acetate, ethyl acetate, isobutyl alcohol and isoamyl alcohol. The absorption spectra of the organic layer are similar to one another, having two peaks—320 and 460 $m\mu$ if hydrazine has been used, and 335 and 468 $m\mu$ if SnCl_2 has been used. Their extinction coeff. are dependent on the solvents, but are proportional

to the concn. of Mo ($< 20 \mu\text{g}$ per 5 ml) when extracted from *N* H_2SO_4 soln. Appreciable interference results from other heavy metals, including Fe^{III} , Co, Cu, V and W.

K. SAITO

2716. The simultaneous photometric determination of molybdenum and tungsten in silicate rocks. P. G. Jeffery (The Geological Survey of Uganda, P.O. Box No. 9, Entebbe, Uganda). *Analyst*, 1956, 81, 104-109.—The silicate rock is fused with NaOH and NaNO_3 , the leached extract is filtered, the insol. matter is discarded, and the filtrate, after removal of SiO_2 in the usual way, is treated with ethanolic benzoin α -oxime soln. and is repeatedly extracted with chloroform. The extract, after removal of chloroform in a Kjeldahl flask, is fumed with H_2SO_4 with addition of HNO_3 and finally of HClO_4 . After dilution, a FeCl_3 soln. is added followed by a toluene-3:4-dithiol reagent (prep. described). After being heated in boiling water for 1 hr. the mixture is acidified, treated with the toluene-3:4-dithiol reagent and set aside for 1 hr. The cooled soln. is extracted with a definite vol. of light petroleum and the extinction of the extract is measured at 630 $m\mu$ and 680 $m\mu$. Two simultaneous equations of the form $E = a(\text{MoO}_3) + b(\text{WO}_3)$ determine the concn. of MoO_3 and WO_3 , the constants *a* and *b* in each being determined experimentally with standard soln. of Mo and W. The method is applicable if the ratio of the contents of the two metals does not exceed ≈ 1 to 12, otherwise Mo must be separated by the method of Allen et al. (*Brit. Abstr. C*, 1953, 302).

A. O. JONES

2717. Amperometric determination of tungsten in ferrotungsten. N. M. Degterev. *Zavod. Lab.*, 1956, 22 (2), 167-168.—The sample (2.5 g) of ferrotungsten in a platinum dish is treated with 10 ml of HF and then dropwise with conc. HNO_3 until the alloy is completely decomposed. Dil. H_2SO_4 (1 + 2) (25 to 30 ml) is added and the soln. is evaporated to fumes. The liquid containing pptd. H_2WO_4 is transferred to a beaker and neutralised with a 30 per cent. NaOH soln., followed by 100 ml in excess. The soln. of tungstate is diluted to 500 ml in a calibrated flask, set aside for the ppt. of $\text{Fe}(\text{OH})_3$ to settle and then filtered. An aliquot portion (20 ml) of the filtrate is made slightly acid to litmus with dil. acetic acid (1 + 3) (excess > 2 ml), and the cooled soln. is treated with 100 ml of water and 3 g of sodium acetate and titrated amperometrically with 2 per cent. 8-hydroxyquinoline in 10 per cent. acetic acid at 1.4 V. The titrant is added in 1-ml portions.

G. S. SMITH

2718. A new volumetric method for the estimation of uranium (VI) through photochemical reduction with alcohol. G. Gopala Rao, V. P. Rao and N. C. Venkatamma (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, 150 (3), 178-185.—The method described is superior to that in which a Jones or a silver reductor is used. Soln. of U^{VI} are quant. reduced to U^{IV} by ethanol when exposed to sunlight or to the light of a high-pressure mercury-vapour lamp for at least 30 min. For speedy reduction, the soln. must have a min. concn. of H_2SO_4 of 1 *N*. Although the rate of reduction increases with the concn. of ethanol, a large excess must be avoided. The oxidation back to U^{VI} is accomplished with standard sodium vanadate soln. since other oxidising agents oxidise the excess of ethanol. No interference results from the presence

of F' and PO_4''' , unless the H_2SO_4 concn. is low, whilst $HClO_4$ or H_3PO_4 (in concn. $> 4N$) may replace the H_2SO_4 . Arsenates do not interfere, but Cl' and Br' completely inhibit the photochemical reduction, and oxalate slightly retards the reaction. *Procedure*—Volumes of UVI soln. (0.5 to 6 ml containing 0.028 to 0.078 millimole of UVI) are mixed with 5 ml of M ethanol soln. and 5 ml of $5N$ H_2SO_4 , and then diluted to 25 ml. The soln. are exposed in glass vessels to a mercury-vapour lamp for ≈ 1 hr. and then titrated with 0.025 N sodium vanadate soln. Diphenylbenzidine or N -phenylanthranilic acid is used as indicator, and 5 ml of H_3PO_4 and 2 ml of N oxalic acid are added as catalysts. J. H. WATSON

2719. Determination of fluorine by means of amperometric titration with ferric iron. Sôichirô Musha and Toshimasa Higashino (Faculty of Eng., Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 128-133.—The amperometric titration (0.0 V vs. the S.C.E.) of F' with Fe''' was studied by the use of a rotating platinum electrode. For the regulating soln., 50 per cent. ethanol (pH 2.2 to 3.4) containing HCl and Na acetate was the most satisfactory. Since most metal ions have $E_1 < 0.0$ V vs. the S.C.E., they do not interfere with the titration unless a stable fluoride complex is formed. Appreciable interference is given by oxalate, arsenate and copper. An aq. soln. containing ≈ 10 mg of F' is neutralised to phenolphthalein and treated with 3 N Na acetate (2.5 ml), 6 N HCl (6 ml), ethanol and water to produce the regulating soln. The soln. is placed in a H-type cell and amperometrically titrated with 0.1 N Fe''' soln., with a platinum electrode (800 r.p.m.). Since the fluoride complex of Al or Th is more stable than that of Fe , this method can be modified for the titration of F' with standard soln. of Al or Th , Fe''' being used as an amperometric indicator. K. SAITO

2720. The determination of fluorine by a direct alkalimetric titration after distillation. M. M. Vinnik. *Materialy Obmenu Opytom. Nauch. Inst. Udobr. i Insektofungitsidam*, 1954, (6), 13-22; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,558.—To determine F' , mix the weighed sample [CaF_2 , NaF , K_2SiF_6 (0.1 g), apatite (1.5 to 1.8 g), superphosphate (3 to 5 g)] with 30 ml of H_2SO_4 (1:2) and 0.5 to 1 g of quartz sand, and distil off H_2SiF_6 at 98° to $250^\circ C$, collecting 17 to 20 ml of distillate in a receiver containing KCl soln. The presence of H_3BO_3 , colloidal SiO_2 and salts of Al slows down the distillation. Adjust the pH of the distillate to 3.5 with $NaOH$ soln. in the presence of three drops of mixed indicator [0.1 per cent. alcoholic dimethyl yellow soln. - 0.1 per cent. methylene blue soln. (1:1)]. Heat the soln. to boiling point (clear green soln.), add 0.5 ml of 1 per cent. phenolphthalein soln., and titrate with 0.1 N $NaOH$ to a faint pink. Heat, and if the colour changes, titrate again to a permanent pink. The time of determination is 1.5 to 2.5 hr. C. D. KOPKIN

2721. Quantitative determination of fluorine with the aid of radioactive phosphorus. J. M. P. Cabral and H. Götze (Max Planck Inst. Chemie, Mainz, Germany). *Z. Naturforsch.*, 1955, **10b** (8), 440-442.—Radioactive zirconium phosphate reacts with fluorides to give zirconium fluoride and an equivalent amount of radioactive ^{32}P as H_3PO_4 , which is separated from excess of zirconium phos-

phate by paper chromatography. *Procedure*—Apply to the paper 2 μ l of 3.5 per cent. zirconium chloride solution and add 4 μ l of 4 per cent. H_3PO_4 (having an activity of 2×10^6 counts per min. per mg of P). Allow the spot to dry. Chromatograph in ascending fashion with water - isopropyl alcohol (3:7) in which 5 g of trichloroacetic acid are dissolved per 100 ml. Allow 14 hr. for the run. In this operation the excess of H_3PO_4 is removed from the zirconium phosphate ppt. Dry the paper and apply 2 μ l of the fluorine-containing solution to the original spot. Elute the dried paper with the same solvent mixture for 2 hr. to remove the liberated H_3PO_4 to a position midway between the two existing spots. The area containing the liberated H_3PO_4 is eluted with inactive H_3PO_4 and the eluate is submitted to the counter. The fluorine content is calculated from the result. There is no interference from Na , K , Mg and Ca , but Fe prevents the full liberation of H_3PO_4 by the fluorine. E. KAWERAU

2722. Determination of hydrofluoric acid in nitric - hydrofluoric acid mixtures. Development of a field test. D. H. Wayman (Bell Aircraft Corp., Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 865-867.—This colorimetric method is a development of an A.S.T.M. procedure. It comprises (i) adjustment of the pH of the sample aliquot and water blank, with Na alizarinsulphonate indicator, (ii) titration with $Th(NO_3)_4$ to the characteristic red - purple colour of the lake, (iii) addition of the same amount of $Th(NO_3)_4$ to the blank, and (iv) titration of the blank with standard NaF until the colour matches that of the sample aliquot. Interfering cations are first removed by an ion-exchange column of Amberlite IR-120 (H), a max. total contamination of 14 mg being removed in this way. Less than 1 hr. is required for the total analysis. The accuracy for aliquots containing 8 mg of F' was within ± 0.1 mg. K. A. PROCTOR

2723. Determination of fluoride ions by titration with potassium aluminium sulphate solution. R. Schliebs (Anorg.-chem. Inst., Univ. Münster, Westf., Germany). *Z. anal. Chem.*, 1956, **150** (5), 321-328.—A mixture of bromocresol purple and bromothymol blue is recommended as indicator for the neutralisation of fluoride samples before titration with $KAl(SO_4)_2$ in an aq. alcoholic medium. Potentiometric titration confirms and explains the blank value reported by Rinck (*Bull. Soc. Chim. France, Mém.*, 1948, **15**, 305) when a mixture of methyl red and methylene blue is used as indicator in the fluoride - aluminium titration. The error in the titration to a visual end-point is $\approx \pm 0.5$ per cent. The cations Na^+ and K^+ do not interfere, nor the anions of strong acids, but Cu^{++} , Ni^{++} and the anions which have a buffering effect must be absent. A. R. ROGERS

2724. Determination of fluoride in chromium-plating solutions. J. P. Branciaroli and J. G. Coleman (Diamond Alkali Co., Painesville, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 803-804.—The method described is more than sufficiently accurate for controlling chromium-plating baths. Sodium hydroxide is added to the sample in excess of that required to convert the chromic acid into Na_2CrO_4 , and at this point metal contaminants are precipitated as the hydroxides. An excess of $AgNO_3$ is then added to precipitate the CrO_4^{--} as the silver salt, and after filtration a colourless solution is obtained which can be titrated with

$\text{Th}(\text{NO}_3)_4$ in the presence of a buffer to control the pH. The determination can be completed in about 20 min. by an experienced analyst.

K. A. PROCTOR

2725. Semi-micro method for the determination of chloride. P. Blanc, P. Bertrand and L. Liandier. *Chim. Anal.*, 1956, **38** (5), 156-157.—A speedy and simple nephelometric method for the determination of Cl^- in the range 0 to 20 mg per litre is described. The ppt. obtained by the addition of AgNO_3 is maintained in suspension by a 20 per cent. solution of Tween-20. After 30 min. of frequent agitation at 40°C , measurement of the turbidity of the resulting solutions is made. Beer's law is obeyed over the range studied. The application of the method to the determination of Cl^- in potable and mineral waters, biological fluids and wines is described. The accuracy of the method is said to be comparable with that of volumetric methods.

K. A. PROCTOR

2726. An electrometric method for the determination of small quantities of chlorides. P. M. Deschamps (11 rue Pierre Curie, Paris, V). *Bull. Soc. Chim. France*, 1956, (1), 126-128.—Small quantities of chlorides are titrated in aq. or aq. acetone solutions by the dead-stop technique, with silver or gold amalgam as one electrode and silver as the other. A small quantity of added H_2SO_4 increases the sensitivity. Solutions containing as little as $91\ \mu\text{g}$ in 25 ml are satisfactorily titrated, but for such dilute solutions it is necessary to plot the curve of current against vol. of added AgNO_3 solution and determine the end-point graphically. The possibility of extending the method to the determination of bromide and iodide is discussed.

E. J. H. BIRCH

2727. Rapid method for determination of iodide in the presence of chloride and bromide. J. Bitskei (Inorg. Chem. Inst., Tech. Univ., Budapest). *Z. anal. Chem.*, 1956, **150** (4), 267-271.—Iodide is determined in alkaline solution (pH 10 to 11) at 50° to 60°C by oxidation with an excess of OCl^- to IO_3^- ; the IO_3^- are treated with $\text{Na}_2\text{S}_2\text{O}_3$ (equiv. to the OCl^-) and the excess of $\text{Na}_2\text{S}_2\text{O}_3$ is titrated with NaOCl (brasilin indicator). The oxidation is catalysed by Br^- . Thus 15 to 50 mg of KI are determined with an accuracy within $\pm 0.1\ \text{mg}$. *Procedure*—Add to the I^- soln. (10 to 40 mg of I^-), KBr (0.2 g), KHCO_3 (2.3 g) and H_2O (5 to 10 ml), and warm to between 50° and 60°C . Add from a burette an excess of 0.1 N NaOCl , set aside the warm soln. for 1 to 1.5 min. (not longer), then add 3 per cent. NaOH (10 ml) and 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (exactly equiv. to the NaOCl). Add 1 per cent. alcoholic brasilin (1 drop) and 5 per cent. KI (1 drop) and titrate slowly with 0.1 N NaOCl to a yellowish-green end-point.

J. P. STERN

2728. Spectrocolorimetric analysis. Some applications in ferrous metallurgy. E. Sory (S.N.C.F. Lab.). *Chim. Anal.*, 1956, **38** (4), 125-129.—The various physical and chemical considerations that bear on spectrochemical analysis are discussed, and the points are illustrated by reference to the determination of Ni , Mn and Mo in steel. A warning is given on the use of methods that have been introduced too quickly without a sufficiently detailed investigation.

J. H. WATON

2729. Permanganimetry of ferrous ion without addition of acid. F.-E. Raurich Sas and M. Castillo Cofiño (Alonso Barba Inst., Barcelona). *Inf.*

Quim. Anal., 1956, **10** (1), 9-11.—From a study of the interference of Fe^{2+} in the oxidation of gluconates with KMnO_4 , the oxidation of Fe^{2+} by KMnO_4 under acid-free conditions as used in the oxidation of gluconates is shown to proceed according to the equation $6\text{KMnO}_4 \rightarrow 6\text{MnO}_2 + 3\text{K}_2\text{O} + 9\text{O}$.

L. A. O'NEILL

2730. Spectrophotometric determination of iron in strong alkali media. 4:7-Dihydroxy-1:10-phenanthroline as iron (II) organic chelation reagent. A. A. Schilt, G. F. Smith and A. Heimbuch (Illinois Univ., Urbana, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 809-812.—The spectrophotometric determination of traces of Fe^{2+} by chelation with Snyder's reagent (4:7-dihydroxy-1:10-phenanthroline) is described. The reagent is unique for its stability in strongly alkaline media and may therefore be used for the specific determination of iron impurities in alkali hydroxides, alkali carbonates, reagent aq. NH_3 , alkaline-earth oxides and hydroxides, and alkaline phosphates. Of a large number of anions tested, only cyanide ($>2\ \text{p.p.m.}$), tartrate ($>1000\ \text{p.p.m.}$) and thiosulphate ($>10,000\ \text{p.p.m.}$) interfered significantly. Under the conditions described, Ni , Mo , Ti and Zr do not form coloured complexes in the visible spectrum range; and alkaline-earth metals, although precipitating if present in sufficient concn., do not interfere. The coloured complex exhibits max. absorption at $520\ \text{m}\mu$ and Beer's law is obeyed for concn. of $\text{Fe}^{2+} >6\ \text{p.p.m.}$ The determination of Fe in glass sand is given as an example of the application of the method; for 11 replicates (containing 0.0485 per cent. of Fe) the standard deviation was 0.0002 per cent.

K. A. PROCTOR

2731. Spectrophotometric determination of iron in tin and lead alloys with o-phenanthroline. Kazuo Ota (Toyota Motor Co. Ltd., Koromo, Aichi Prefecture). *Japan Analyst.*, 1956, **5** (1), 3-7.—The A.S.T.M. method for determining iron (<0.1 per cent.) in tin and lead alloys was modified for a more rapid analysis. Sn , Sb and As are removed by heating with HBr and H_2SO_4 . The adsorption of Fe by PbSO_4 is negligible. In the presence of Zn and Cu , Fe is co-pptd. with $\text{Al}(\text{OH})_3$ in aq. NH_3 soln. A linear working curve is obtained for 0.01 to 0.30 mg of Fe^{2+} in 100 ml of acetate buffer (pH 4) containing hydroxylamine hydrochloride (1 per cent., 3 ml) and o-phenanthroline (0.2 per cent. aq. soln., 5 ml). The error is <0.002 per cent. for ≈ 0.05 per cent. of Fe . *Procedure*—The sample ($<1\ \text{g}$) is decomposed with H_2SO_4 (10 ml) and cooled, then heated with HBr (sp.gr. 1.38 to 1.48) (10 to 15 ml) at 200° to 250°C in a current of air. The cooled residue is heated with HNO_3 (2 ml) to white fumes for 2 min., and again cooled and dissolved in water (50 ml). The soln. is filtered, evaporated to 5 ml, neutralised with aq. NH_3 soln. to o-nitrophenol and transferred to a measuring flask (100 ml) with H_2SO_4 (2 ml) for colorimetry.

K. SAITO

2732. Spectrochemical investigations for the micro-analysis of steel structure. S. Eckhard, W. Koch and C. Mahr (Max-Planck-Inst. für Eisenforschung, Düsseldorf, Germany). *Angew. Chem.*, 1956, **68** (8), 296-302.—Many trace elements can be spectrometrically detected and determined in isolated structure elements of steel which cannot be studied by microchemical methods. Techniques have been evolved to manipulate samples weighing as little as 50 μg .

A. R. ROGERS

2733. A comparison of three methods of plate calibration and evaluation for routine spectrographic analysis of low-alloy steels. H. T. Shirley, A. Oldfield and H. Kitchen (Firth-Brown Res. Lab., Sheffield, England). *Spectrochim. Acta*, 1956, **7** (6), 373-386.—Experimental evidence has shown that, with individual plate calibration, an improvement of the order of 20 per cent. in analytical accuracy may be expected from the use of either (i) a method based on the direct relation of densitometer readings to log. (relative intensity) or (ii) the Kaiser-Seidel transformation (P value) technique for straightening the plate-response curve. About 30 per cent. of the improvement is the direct result of individual plate calibration technique as compared with the batch method of plate calibration. D. G. HIGGS

2734. Rapid qualitative analysis of special steels with Complexone III. S. Arribas Jimeno and G. Ortiz Redondo (R.E.N.F.E., Central Laboratory, Madrid). *Inf. Quim. Anal.*, 1956, **10** (1), 1-8.—The following scheme is outlined. The steel is dissolved in hot dil. H_2SO_4 . Tin is recognised by luminescence after treatment with Zn and HCl, W is pptd. as WO_3 with conc. HNO_3 , and the remaining metals are detected in the filtrate. Part of the filtrate is treated with Complexone III (EDTA, disodium salt) and tests are carried out for Cr, Ti, V and Cu. Another part is treated with excess of NaF, and tests are made for Ni, Co and Mn. Molybdenum is detected with K ethyl-xanthate. L. A. O'NEILL

2735. The determination of low carbon contents in steel by multiple factor weight combustion. B. Bagshawe and R. H. Pinder (Brown-Firth Res. Lab., Princess St., Sheffield). *Analyst*, 1956, **81**, 153-159.—To enable determinations of C in low-carbon steel to be made to third-figure accuracy the combustion unit has been enlarged to accommodate six times the normal factor weight (i.e., 6×2.729 g), and the absorption system for CO_2 has been reduced in wt. so that the CO_2 can be determined with greater precision. The apparatus is described and illustrated and details of the method are given. The normal tolerance of ± 0.01 per cent. has been reduced to ± 0.002 per cent. The procedure is applicable to all classes of low-carbon steel and particularly to the extra-low-carbon grades (< 0.05 per cent. of C) of stainless and high-chromium-nickel austenitic steels. A. O. JONES

2736. The determination of small amounts of carbon in steel by low-pressure analysis. R. M. Cook and G. E. Speight (B.I.S.R.A., Hoyle Street, Sheffield, England). *Analyst*, 1956, **81**, 144-152.—The apparatus described and illustrated is a modification of that of Wells (*Brit. Abstr. C*, 1951, 203) and consists essentially of a combustion furnace, freezing trap and measuring gauge. The sample of steel millings or drillings is mixed with a specially prepared red-lead flux and burnt in a stream of purified O. After removal of solid particles, partial dehydration by $Mg(ClO_4)_2$, removal of sulphur compounds by pptd. MnO_2 , and final dehydration by $Mg(ClO_4)_2$ and P_2O_5 , the CO_2 is removed from the oxygen stream by means of a multiple-coil freezing trap immersed in liquid O. Finally the CO_2 is volatilised by removal of the freezing trap and warming, and is measured in a modified form of the Toepler and McLeod gauge system. Blank determinations, which are consistent and low, are made

with the red lead only. Under the condition described, no CO occurs in the stream of O and CO_2 . The precision is ± 0.0001 per cent. of C up to 0.036 per cent. of C and is slightly greater with higher contents of C. A. O. JONES

2737. Determination of magnesium in iron. R. Reichert (Montan. Hochschule, Leoben, Austria). *Z. anal. Chem.*, 1956, **150** (4), 250-253.—Magnesium (0.01 to 0.1 per cent.) is determined compleximetrically in cast iron containing traces of Mn and Zn; Fe is pptd. with H_2S , Mn is masked with triethanolamine, and other metals are complexed with KCN. Interfering oxidising agents are reduced with ascorbic acid (I). The Mg is titrated with EDTA (disodium salt) in the presence of Eriochrome black T as indicator. A single determination takes 45 min. The accuracy on 0.2 to 5 mg of Mg in 1 to 10 g of Fe is within ± 1 per cent. *Procedure*—Dissolve the Fe (containing 0.1 mg of Mg) in HCl and some HNO_3 , add an excess of aq. NH_3 and 1 to 2 g of NH_4Cl , and then pass H_2S . Filter off the solid and wash it. Treat the warm filtrate and washings with I (1 g), 10 per cent. KCN (10 ml) and aq. triethanolamine soln. (1:1) (2 ml). The final vol. should be ≈ 200 ml. Add more I (0.5 g), heat the solution, add solid Eriochrome black T, adjust to pH 10 with aq. NH_3 , and titrate at 60° C with 0.01 M EDTA (disodium salt) to a blue end-point. J. P. STERN

2738. Photocolorimetric determination of silicon in ferrous metals. E. I. Fogel'son (I. V. Stalin Automobile Works). *Zavod. Lab.*, 1956, **22** (2), 163-165.—The optimum conditions are studied for determining silicon in steel and cast iron by a method based on the reduction of molybdosilicate by $FeSO_4$ in the presence of ammonium oxalate (added to destroy the molybdophosphate complex). Addition of $FeSO_4$ should be made immediately after the addition of oxalate, since otherwise the unreduced molybdosilicate complex may be partially destroyed. Urea is added to prevent the destruction of the blue reduced complex by oxides of N. *Determination of Si in carbon steel*—The sample (0.1 g) is dissolved in 10 ml of dil. H_2SO_4 (1 + 8). The solution is heated with 5 ml of dil. HNO_3 (1 + 4) until oxides of N are removed, then made up to 100 ml with water in a calibrated flask, after filtration, if necessary. Two 5-ml aliquot portions are placed in separate 50-ml flasks and to each are added 20 ml of water. Ammonium molybdate solution (5 per cent.) (5 ml) is added to one flask and after 3 min. both solutions are treated with 10 ml of 3 per cent. ammonium oxalate or oxalic acid soln. The ppt. formed by the ammonium molybdate dissolves, and ferric sulphate soln. (6 per cent.) (5 ml) is added to each soln., followed by water to the mark. The colour intensities are measured, with a red filter, by the compensation method in 20-mm cells. *Determination of Si in cast iron*—The sample (0.1 to 0.05 g) is dissolved as for steel but, if 0.05 g is taken, an addition of 2 ml of iron alum soln. [54 g of the alum and 1 ml of H_2SO_4 (1 + 1) in 250 ml of water] is made. *Determination of Si in heat-resistant steel*—The sample (0.1 g) is dissolved in a mixture of 15 ml of dil. HCl (1 + 2) and 5 ml of dil. HNO_3 (1 + 2). G. S. SMITH

2739. The colorimetric determination of phosphorus in steel and copper-base alloys. W. T. Elwell and H. N. Wilson (Res. Dept., I.C.I. Ltd., Billingham Div., Co. Durham, England). *Analyst*,

1956, **81**, 136-143.—In the colorimetric method described the steel millings are dissolved in HCl and HNO₃ and the soln. is fumed with HClO₄. The soln. is reduced with SO₂, boiled with dil. HNO₃ and then treated with an ammonium vanadate and molybdate reagent (prep. described), and the molybdovanadophosphoric acid formed is extracted with isoamyl alcohol. The extinction of the yellow extract is measured at 426 m μ and corrected for a reagent blank. For copper-base alloys the use of HClO₄ and addition of SO₂ are omitted, otherwise the method is similar. Slight modifications of the method for certain types of steel are indicated. A. O. JONES

2740. Influences of arsenic on the determination of various elements in iron and steel. **III. Studies on the determination of titanium and molybdenum.** H. Gotô and S. Watanabe. *Nippon Kinzoku Gakkai-Shi*, 1955, **19** (1), 12-14.—In the determination of Ti by the volumetric method in which zinc amalgam and ferric sulphate soln. are used, As produces high results when Ti is not separated, but does not interfere when Ti is separated as phosphate, or in the gravimetric method. Arsenic produces high results in the volumetric method for Mo based on separation by NaOH, but does not affect the gravimetric method.

J. IRON & STEEL INST. ABSTR.

2741. The analytical application of -onium compounds. **VIII. Spectrophotometric determination of cobalt as tetraphenylphosphonium cobaltothiocyanate.** Mutsuaki Shinagawa, Hiroshi Matsuo and Rikusei Kohara (Chem. Dept., Faculty of Sci., Hiroshima Univ., Higashisenda-machi, Hiroshima). *Japan Analyst*, 1956, **5** (1), 29-32.—Complex formation of Co⁺⁺ with I in KSCN soln. was studied by means of the polarogram of Co⁺⁺. The pptn. of Co is quantitative between pH 2 and 7. The blue ppt. is soluble in chloroform and the extinction coeff. (620 m μ) of the CHCl₃ layer is proportional to the amount of Co within the range 3 to 30 μ g per ml. The accuracy is within ± 5 per cent. No interference results from comparable amounts of elements other than Fe^{III}, Cu and Bi. K. SAITO

2742. Determination of nickel in oxidised films on nickel metal. B. D. Brummet and R. M. Hollweg (Thos. A. Edison, Inc., West Orange, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 887-888.—In a rapid spectrophotometric determination, a 0.5 per cent. KCN solution is used to remove the oxidised film and is specific for this film as long as oxygen is excluded from the solution. For accurate work, a nitrogen box is used to provide an oxygen-free atmosphere, but good results can be obtained by flushing the solution with N before addition of the sample and then continuing the flushing during the contact period. The Ni is determined by measurement of the extinction of the nickel cyanide complex at 268 m μ . Beer's law was obeyed for 2×10^{-7} to 25×10^{-7} g of Ni per ml.

K. A. PROCTOR

2743. Determination of nickel, chromium and molybdenum using the Spekker absorptiometer. J. Winning and S. Miller (Albion Motors Ltd., Glasgow, Scotland). *Metallurgia, Manchester*, 1956, **53**, 50-52.—The substitution of other reagents for HClO₄ and AgNO₃ for routine absorptiometric examination of alloy steels is shown to be more economical both in cost and time and to avoid inconvenience due to heavy fumes. The reagents

are—Spekker acid (150 ml of H₂SO₄ and 150 ml of H₃PO₄ in 1 litre of water) (I), saturated aq. KMnO₄ (II), and (NH₄)₂S₂O₈ in the form of 0.75-g "Analoid" pellets (III). A typical procedure is to dissolve 1 g of steel in 40 ml of I, oxidise with a few drops of HNO₃ and fume to remove carbides and excess of HNO₃. The mixture is then diluted to 100 ml, heated to boiling point, and sufficient II is added dropwise to give a permanent clear pink colour. Two pellets of III are added and, when the action is complete, three or four drops of HCl. If Cr is present, the solution is a clear orange-yellow. It is further diluted to 200 ml and the Cr is measured directly in the absorptiometer, with a blank obtained by the same treatment of 1 g of pure Fe. Nickel is estimated by taking 100 ml of the same solution, diluting to 250 ml, and using 10 ml for colour and blank. The brownish-red nickel colour with ammoniacal dimethylglyoxime and iodine is then developed and difference readings are taken in the absorptiometer. To estimate Mo, two 20-ml portions of the steel solution are treated with, successively, 10 ml each of 50 per cent. aq. H₂SO₄, 10 per cent. aq. KBr, 10 per cent. aq. KSCN, and 10 per cent. SnCl₂ containing 5 per cent. of HCl. The whole is then made up to 100 ml. The blank contains all the reagents except KSCN and, after standing for < 5 min., the difference reading is measured. Calibration curves are given for Cr, Ni and Mo. Each is linear and passes through the origin. In the absorptiometer, the following cells and filters are used: for Cr, 2-cm cell and violet No. 601 filter; for Ni, 1-cm cell and green No. 604 filter; for Mo, 4-cm cell and green No. 604 filter.

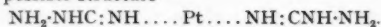
S.C.I. ABSTR.

2744. Analytical application of the reaction resulting in the formation of di(acetamido)platinum. V. F. Barkovskii and L. M. Kul'berg. *Izvest. Sektora Platiny I.O.N.Kh., Akad. Nauk SSSR*, 1955, (29), 141-148; *Ref. Zhur., Khim.*, 1955, Abstr. No. 49,095.—Acetamide reacts with K₂PtCl₆ to give bluish-violet di(acetamido)platinum, Pt(NHCOCH₃)₂.H₂O. With a 200-fold excess of acetamide, the reaction is quant. at 100° C in 15 to 20 min. To determine Pt in various materials, the Pt is first obtained in the form H₂PtCl₆. KNO₃ is added to ppt. K₂PtCl₆, and the liquid containing the ppt. is reduced at 100° C for 30 to 40 min. with saturated K oxalate soln. It is then treated with acetamide soln. and heated with Ca(NO₃)₂ soln. and CaCO₃ to remove the excess of oxalate and neutralise the soln. The colour intensity at 660 m μ is measured after the soln. has been centrifuged. Interference is caused by Cu⁺⁺, Fe⁺⁺⁺, Al⁺⁺⁺, Ag⁺, Au⁺⁺⁺, Pd⁺⁺, Ir⁺⁺⁺, Rh⁺⁺⁺, Ru⁺⁺⁺, Cl⁻ and Br⁻, but not by SO₄⁼⁼ and NO₃⁻. The calomel method can be used to separate Pt from Cu, Fe, Ni and Al.

G. S. SMITH

2745. The reaction between potassium chloroplatinite and thiosemicarbazide and its analytical use. V. F. Barkovskii and L. M. Kul'berg. *Izvest. Sektora Platiny I.O.N.Kh., Akad. Nauk SSSR*, 1955, **29**, 149-162; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,264.—The reaction between Pt and thiosemicarbazide in alkaline medium is studied. It is established that the formation of the intense blue colours of such soln. is connected with the formation of a definite chemical compound, and not with a colloidal soln. of Pt. In this reaction, 1 mol. of chloroplatinite and 2 mol. of thiosemicarbazide take part to give a compound having

the possible structure—



A colorimetric extraction method has been evolved to determine Pt with thiosemicarbazide in a wide range of concn. (100 to 1000 μg per ml). No interference is caused by considerable quantities of Au, Ir and Rh. A method is described for the determination of Pt in iridium preparations and other materials.

C. D. KOPKIN

2746. Study of the iodide titration for determination of palladium. R. N. Rhoda and R. H. Atkinson (International Nickel Co., Bayonne, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 535-537.—A study has been made of the volumetric method for the determination of Pd in Pd-rich alloys based on the titration of PdCl_2 with KI and with the ppt. as its own indicator (cf. *Analyst*, 1954, **79**, 368). The accuracy is within ± 0.25 per cent., and is not affected by the presence of <5 per cent. of Bi, Co, Cu, Cr, Ir, Fe, Mn, Mo, Ni, Pt, Rh, Ru, Sn and W; Au and Ag interfere, but can be removed before titration. The small error introduced by the solubility of PdI_2 is avoided by direct standardisation of the reagents against pure palladium metal. To avoid reduction of Pd^{++} to Pd, the FeSO_4 must not be added to the sample solution until after the HCl has been added and the mixture cooled to room temp.

A. R. ROGERS

2747. Decomposition of minerals and ores by ammonium salts. P. M. Isakov. *Vestnik Lenin-grad. Univ.*, 1955, (4), 117-133; *Ref. Zhur.*, *Khim.*, 1955, Abstr. No. 49,105.—The decomposing action on minerals and ores of NH_4Cl , NH_4Br , NH_4F , NH_4I , NH_4NO_3 and some mixtures of these salts is studied. The most effective for both quant. and qual. analysis are NH_4Cl , NH_4NO_3 and a mixture of between 2 and 3 parts of NH_4Cl to 1 part of NH_4NO_3 (solid aqua regia). Methods of oxidising S by a mixture of NH_4Br and NH_4NO_3 and decomposing silicates by a mixture of NH_4F and NH_4NO_3 are described. Decomposition by ammonium salts takes only 5 to 7 min.

G. S. SMITH

2748. Quantitative and qualitative determination of the composition of clays, bauxites and certain other minerals by the method of heating. V. P. Astaf'ev. *Issledovanie Mineral'nogo Syr'ya*. Published by Gosgeoltekhizdat, 1955, pp. 85-93; *Ref. Zhur.*, *Khim.*, 1955, Abstr. No. 49,209.—The determination of their loss in weight on heating can be used to establish the approx. composition of clays, bauxites and some other minerals. At 350° to 400°C , oxidation and burning of organic components occurs, at 550° to 600°C there is loss of water of hydration, and above 600°C there is loss of CO_2 and SO_4^{--} and also halogens. Samples are air-dried for 3 or 4 days; then 3 to 5 g are heated, first at 100° to 110°C for 4 to 5 hr. then at 400° to 500°C for 2 hr., followed by heating at 800°C (or in the absence of carbonates and sulphates at 600° to 700°C). Tables showing losses in weight for various materials at various temp. are given.

G. S. SMITH

2749. Phase analysis of gypsum-bearing dolomites. M. A. Popov (Central Lab. W. Siberian Geological Dept.). *Zavod. Lab.*, 1956, **22** (2), 157-160.—Selective extractions are described for determining

chlorides, sulphates and carbonates in gypsum-containing dolomites. Magnesium chloride is determined from the content of Mg and Cl in an ethanol extract. Sodium chloride is determined from the difference between the total Cl and that in the ethanol extract.

G. S. SMITH

See also Abstracts 2610, 2611, 2615, 2616, 2617, 2620, 2621, 2838, 2907.

3.—ORGANIC ANALYSIS

2750. Use of mass spectrometry in analysis of organic substances. J. D. Waldron (Metropolitan-Vickers, Trafford Park, Manchester, England). *Erdöl u. Kohle*, 1955, **8** (12), 889-895.—The arrangement and operation of a mass spectrometer now available as a complete unit are outlined, with examples of its application. Repeat analyses of mixtures made up with known proportions (5 to 10 mol. per cent.) of H, N, CO_2 , and 12 paraffins and olefins (1 to 4 C) had standard deviations for individual components which averaged 0.34 mol. per cent. and differed from the actual values by >0.5 mol. per cent. Accuracy can be improved, and more complex mixtures analysed, by comparison of individual spectral peaks with those of a series of known synthetic mixtures, but, owing to the similarity of their ionic mass distributions, isomers are not easily distinguished and recourse should be had to infra-red spectra. Impurities in a gas can be identified and estimated when present in quantities which depend on the spectral differences, but which may in favourable cases be as low as 0.001 per cent. The experimental work occupies 5 to 15 min., and routine calculation of the results is done mechanically. Volatile liquids of v.p. <0.3 mm Hg at atm. temp. can be analysed. For less volatile substances the inlet system is heated ($>350^\circ\text{C}$) and a receiver of greater resolving power is used; e.g., *n*- and *iso*-paraffins, naphthenes, etc., can be determined in lubricating oils and waxes within ± 3 per cent. Non-volatile substances (polymers, proteins, etc.) are pyrolysed and the decomposition products show characteristic spectra from which the composition of the original material may be deduced. Qual. analyses and mol.-wt. determinations can be done on minimal amounts of material since the most frequent ion is the complete charged mol. With high resolution, in the presence of a reference substance, very small mass differences are distinguishable, e.g., the doublet C_6H_7^+ (mass 43.0676) and CH_3CO^+ (mass 43.0322) can be resolved in CO_2 .

A. R. PEARSON

2751. Sealed-tube combustion technique for determination of deuterium in organic compounds. N. R. Trenner, B. H. Arison and R. W. Walker (Merck & Co. Inc., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 530-531.—The usefulness of the standard dynamic combustion method for the determination of deuterium in organic compounds is limited by a marked "memory" effect (cf. *Perkin-Elmer Instruments News*, 1952, **4**, No. 1). A static combustion technique is now described which avoids this source of delay and error, and permits the determination of deuterium concn. in the range of 1 atom per cent. with a precision of ± 1 per cent. in 5- or 10-mg samples. The i.r. spectroscopy is the same as previously described, except that the reference wire-screen is replaced by a metallised glass plate.

A. R. ROGERS

2752. Determination of carbon in organic compounds by the iodic acid decomposition method. Shigeru Ohashi (Kanazawa Univ., Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (8), 585-588.—In this semi-micro, wet-combustion method, the sample (10 to 60 mg) is decomposed by heating with a mixture of KIO_3 and conc. phosphoric acid (89 per cent. orthophosphoric acid heated to 320°C) (cf. *Anal. Abstr.*, 1955, **2**, 2448). The liberated CO_2 is absorbed in 0.1 N NaOH in a special spiral absorber and, after addition of BaCl_2 solution, the excess of NaOH solution is titrated with 0.1 N HCl, to thymol blue. Most of the liberated iodine sublimes on the walls of the reaction vessel, but any that passes out with the gas stream is absorbed in a tube containing $\text{Na}_2\text{S}_2\text{O}_3$ before reaching the NaOH solution. Among organic compounds analysed were oxalic and tartaric acids, arabinose, alanine, urea and methyl red. The accuracy was within ± 2 per cent.

C. A. SLATER

2753. The semi-micro determination of carbon and hydrogen by the rapid combustion procedure. G. Ingram and M. Lonsdale (Courtauld's Ltd., Maidenhead, England). *Chem. & Ind.*, 1956, (15), 276.—The rapid combustion method for the micro-determination of C and H (Belcher and Ingram, *Brit. Abstr. C*, 1950, 386; 1951, 33) is adaptable to semi-micro working (3 to 30 mg) by using an increased oxygen flow-rate of 150 ml per min., with a vaporisation time of 10 min. followed by 5 min. sweeping out. The amount of MnO_2 used to retain the oxides of N must be increased. The blank values vary little with the flow rate.

E. J. H. BIRCH

2754. Combustion method for liquid organic compounds used in the isotope analysis of hydrocarbons. P. Baertschi and M. Thürkaut (Phys. Chem. Inst. Basle Univ.). *Helv. Chim. Acta*, 1956, **39** (1), 79-81.—An apparatus is described for the combustion analysis of liquid organic compounds, particularly suitable for isotope analyses; when used in conjunction with a standard mass-spectrometer, an accuracy of ± 0.02 per cent. is obtained. A full account of the experimental method is given. Combustion is achieved by passing a high-voltage arc (15 kV; 15 mA) inside an enclosed flask containing the organic compound and a $\text{Ba}(\text{OH})_2$ solution.

C. A. FINCH

2755. Determination of nitrogen in nitro and oxime compounds by the iodic acid decomposition method. Shigeru Ohashi (Kanazawa Univ., Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (8), 537-541.—The iodic acid decomposition method for the determination of organic nitrogen (cf. *Anal. Abstr.*, 1955, **2**, 2448) has been extended to the analysis of nitro and oxime compounds. *Procedure*—The sample (10 to 30 mg, sufficient to produce 1 to 5 ml of N) is weighed into a tube and 1 to 1.5 ml of acetone, followed by iron metal powder (50 to 60 mg) and 6 N H_2SO_4 (1 ml), are added. The mixture is heated on a water bath to reduce the organic compound to the corresponding amine. When all the acetone and most of the water have been expelled, conc. phosphoric acid (orthophosphoric acid heated to 320°C) (3 to 5 ml) and KIO_3 (two to three times the theoretical requirement) are added. A gas-introducing tube and a thermometer are fitted into the reaction vessel, the air is displaced with CO_2 , and the apparatus is connected to a nitrometer. The reaction mixture is heated to between 200° and 250°C and when decomposition

is complete the liberated gas is transferred to the nitrometer with CO_2 and the vol. of N is measured in the usual way. The accuracy is within ± 2 per cent.

C. A. SLATER

2756. The reduction of nitro groups in organic compounds before digestion by Kjeldahl's method. R. Belcher and M. K. Bhatti (The University, Birmingham, England). *Analyst*, 1956, **81**, 124-125.—In the method described the reducing agent used is CrCl_3 . For its preparation, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (15 g) is dissolved in 100 ml of 2.5 N H_2SO_4 , mercury containing about 2 per cent. of zinc is added and the liquid is stored under a layer of light petroleum and shaken occasionally during 30 min. In determinations of N, 2 to 2.5 ml of the resulting blue soln. are used, the excess of water being removed by boiling before addition of K_2SO_4 and HgSO_4 .

A. O. JONES

2757. Rapid determination of sulphur in organic compounds by the bivalent tin - phosphoric acid reduction method. Shigeru Ohashi (Kanazawa Univ.). *Bull. Chem. Soc. Japan*, 1955, **28** (9), 645-649.—The procedure for determination of S by the Sn^{II} - H_3PO_4 reagent (*Anal. Abstr.*, 1956, **3**, 2708) is applied to org. S compounds, including methyl orange, sulphaguanidine, and cystine. In some instances (e.g., with thiourea, methionine, acetylmethionine and thionalide) it is first necessary to oxidise the sample with a reagent prepared by heating $\text{K}_2\text{Cr}_2\text{O}_7$ (15 g) with conc. H_3PO_4 (200 g).

S.C.I. ABSTR.

2758. Total sulphur in hydrocarbons by monochromatic X-ray absorption. B. H. Eccleston and M. L. Whisman (Petroleum Expt. Sta., Bureau of Mines, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 545-548.—The determination of total S by X-ray absorption on compounds isolated from petroleum is described. Existing equipment was modified to make calibration simple and rapid, and the results are comparable in precision with those from other X-ray methods and certain chemical methods. Samples can be analysed in about 20 min. Elements other than C and H cause interference which increases with increasing atomic number; N and O, the most likely impurities, thus cause less interference than other elements. The highest oxygen content encountered in a series of 40 fuels was 5100 p.p.m. and resulted in an error of 0.03 per cent. of S.

K. A. PROCTOR

2759. Semi-micro determination of fluorine in organic fluoro compounds. C. Eger and A. Yarden (Sci. Dept., Israel Min. of Defence, Tel-Aviv, Israel). *Anal. Chem.*, 1956, **28** (4, Part 1), 512-514.—A semi-micro method is given for the determination of F in organic compounds, based on ignition with Na_2O_2 in an 8-ml electrically ignited Parr bomb, followed by titration with $\text{Th}(\text{NO}_3)_4$ after removal of the Na by use of an acidic cation exchanger. The mean error is ≈ 0.6 per cent. Other halogens, S, nitro and amino groups do not interfere, and Cl and Br (if present) can be determined simultaneously. *Procedure*—Mix the powdered sample (20 to 60 mg) with sucrose (to a total weight of 200 mg). Add Na_2O_2 (4 g), ignite and cool and extract with water (50 ml). Pass the soln. through a column ($\approx 50\text{ cm} \times 3\text{ cm}$) of Amberlite IR-112 (H^+ form) in a paraffin-coated tube at a rate of 35 drops per min. Collect the percolate in 0.2 N NaOH (10 ml) and dilute to 250 ml with water. To a 10-ml aliquot, add 0.05 per cent. Na alizarinsulphonate

(0.2 ml), 0.1 *N* HCl (dropwise until the colour changes from red to yellow), ethanol (10 ml) and acetate buffer (pH 3.55) (2 ml) and titrate with 0.02 *N* Th(NO₃)₄ soln. The calibration curve is linear in the range corresponding to 0.1 to 0.3 mg of F per 10 ml of final soln. A. R. ROGERS

2760. Applications of nitrometry. X. Determination of carbonyl compounds. Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (3), 351-353.—Carbonyl compounds are pptd. with a known amount of 2:4-dinitrophenylhydrazine (I) in *N* HCl and the excess of I is determined by nitrometry as described in the previous part of this study (*Anal. Abstr.*, 1956, **3**, 2144). The sample (0.1 to 0.6 g) is dissolved in water or ethanol (100 ml), and 1 ml of the soln. is treated with 0.1 per cent. soln. of I in *N* HCl (10.0 ml) on a water bath for a few min. or set aside for \approx 30 min. The time taken for a complete reaction depends on the sample. The ppt. is filtered off and the filtrate is submitted to nitrometry. K. SAITO

2761. Retention volumes of isomeric hexenes and hexanes in gas-liquid partition chromatography using phthalate esters as liquid phase. L. J. Sullivan, J. R. Lotz and C. B. Willingham (Mellon Inst., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 495-498.—The retention volumes for the individual hexene and hexane isomers have been determined by gas partition chromatography on a column of given dimensions, thermal conductivity being used for detection. The stationary phase was *n*-decyl or tetrahydrofurfuryl phthalate on Celite 545, and nitrogen gas was used as carrier. With hexenes, retention volumes were measured at several combinations of temp. and flow rate. Complete separation of a complex mixture is not likely to be achieved by this method alone.

A. R. ROGERS

2762. Bromomethane (methyl bromide). British Standards Institution (Park St., London). B.S. 2710: 1956, 10 pp.—Limits are specified for density, boiling-range, residue and acidity, and methods for their determination are laid down.

E. J. H. BIRCH

2763. Some data on the kinetics of acylation of alcohols by 3:5-dinitrobenzoyl chloride. I. V. Berezin. *Doklady Akad. Nauk, SSSR*, 1954, **99** (4), 563-564; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,591.—3:5-Dinitrobenzoyl chloride (0.29 to 0.27 *M* soln. in dioxan) in the presence of pyridine (17 per cent. by vol.) is used as an acylating agent (in 15 to 20 per cent. excess) for the determination of primary and secondary alcohols and monohydric phenols. Acylation at 20°C takes 10 min. to 2 hr., according to the alcohol. *cyclo*-Hexanol, phenol, and *n*-butyl, *n*-decyl, *n*-octyl and isopropyl alcohols have been determined. The error is ± 1 per cent. C. D. KOPKIN

2764. Practical notes on the determination of aldehydes in rectified spirits by the official method. T. Caldemaisous. (Sucrerie-Distillerie d'Escaudœuvres, Nord, France). *Ind. Aliment. Agric.*, 1955, **72** (12), 797-800.—The purity requirements and methods of preparation of the reagents used in the official method, i.e., basic fuchsin, acetaldehyde ammonia, 50 per cent. aldehyde-free alcohol, and NaHSO₃, are defined, and details of manipulation,

including the preparation of aldehyde standards, and the procedure of analysis, are described.

S.C.I. ABSTR.

2765. The colorimetric determination of formaldehyde with phloroglucinol. G. Almássy and E. Zichy (Med. Univ., Debrecen, Hungary). *Magyar Kém. Foly.*, 1956, **61** (3), 106-109.—In alkaline medium, phloroglucinol (I) and formaldehyde (II) give a red colour which, under the experimental conditions used, is produced after 1.5 to 2 min. and has an extinction max. lasting for 1 min. *Procedure*—Dilute the soln. of II (containing \approx 10 g) a 1000-fold, in two stages. If the content of II is < 4 per cent., only a 100-fold dilution is required. According to the concn. of II, add > 10 ml of the diluted soln. to water (\approx 30 ml) in a 50-ml standard flask. Add the soln. of I (1 per cent., 3 ml) and 10 per cent. aq. NaOH (2 ml, carbonate-free). Dilute to the mark and determine the extinction max. with the use of a Pulfrich photometer, a 0.5-cm cell and an S47 filter. The concn. is determined from a calibration curve, prepared from known soln. of II. A blank must be determined for the reagents. Methanol and acetone in a 100-fold excess do not interfere; formic acid interferes if present in > 5 -fold excess. The max. error is ± 5 per cent. A. G. PETO

2766. 4-Substituted thiosemicarbazides as reagents for the characterisation of aldehydes and ketones. II. 4-Tolylthiosemicarbazide. M. Tisler (Inst. für org. Chem. der Univ. Ljubljana, Murnikova, Yugoslavia). *Z. anal. Chem.*, 1956, **150** (5), 345-347.—4-Tolylthiosemicarbazide can be used as a reagent for characterising aldehydes and ketones (*cf. Anal. Abstr.*, 1956, **3**, 2118). The m.p. of the 4-tolylthiosemicarbazones of 17 aldehydes and 4 ketones are listed. A. R. ROGERS

2767. Peroxytrifluoroacetic acid as a reagent for determination of the carbonyl function in aldehydes and ketones. M. F. Hawthorne (Redstone Arsenal Res. Div., Rohm and Haas Co., Huntsville, Ala.). *Anal. Chem.*, 1956, **28** (4, Part I), 540-541.—Simple aliphatic aldehydes and ketones may be determined by quant. reaction with an excess of peroxytrifluoroacetic acid (I) in 1:2-dichloroethane (II), followed by iodimetric titration of the excess of I. The method is accurate to within ± 10 per cent. in the most unreliable cases studied, and the recovery is usually ≈ 103 per cent. To prepare the reagent, distil trifluoroacetic anhydride (200 g) into dry redistilled II (2 litres) and store in the absence of moisture; the solution is stable indefinitely. Standardise by titration of a 10-ml aliquot with 0.2 *N* NaOH in ice-cold water and add an equivalent amount to 90 per cent. H₂O₂. The reagent is stable for 8 hr. *Procedure*—Dilute the sample (2 g) to 25 ml with II. Cool a 2-ml aliquot in ice, add the I reagent (10 ml) and allow to stand at 25° to 50° C for 30 min. Cool in ice, add ice-cold 25 per cent. H₂SO₄ (25 ml) and KI (1 g) and rapidly titrate with 0.1 *N* Na₂S₂O₃ until the organic layer is colourless. Carry out a blank titration.

A. R. ROGERS

2768. Separation of saturated straight-chain fatty acids. III. Quantitative paper chromatography. O. Perilä (Finland Inst. Technol., Helsinki, Finland). *Acta Chem. Scand.*, 1956, **10** (1), 143-144.—A methanol solution of acids from formic to valeric is esterified with diazomethane and converted into the hydroxamic deriv. The deriv. are chromatographed on paper by the circular method with the

upper layer of *n*-butanol - benzene - water (1:1:1), and the spots are detected by spraying with FeCl_3 soln. (50 g in 1 litre of ethanolic N HCl). The spots are cut out, extracted with FeCl_3 - HCl - water and determined colorimetrically at 520 $\text{m}\mu$. The accuracy is within ± 2 per cent. for concn. of 0.1 to 1 μmole per ml. The deriv. from hexoic to nonoic acids are chromatographed and estimated similarly by using the upper layer of benzene - formic acid - water (1:1:1). The acids from decioic to cerotic are chromatographed on paper saturated with hydrocarbon, with acetic acid - water (9:1) saturated with hydrocarbon as solvent (*cf. Anal. Abstr.*, 1955, 2, 3498). After evaporation of the hydrocarbon, the paper is treated with 1.5 per cent. aq. AgNO_3 and, after removal of excess of Ag^+ , the spots (made visible with a spray of ethanolic *p*-diethylaminobenzylideneternodaniline) are cut out, treated with H_2SO_4 - HClO_4 - HNO_3 and the Ag is determined colorimetrically with dithizone (625 $\text{m}\mu$). For quant. estimation, amounts of 0.2 to 2 μmoles of each acid give an accuracy within ± 5 per cent. Some of the R_F values are quoted.

E. J. H. BIRCH

2769. An improvement in the determination of non-volatile organic acids. G. L. Dernovskaya-Zelentsova. *Trudy Vsesoyuz. Nauch. Issledovatel. Inst. Khlebopek. Prom.*, 1955, (6), 188-192; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,322.—An improvement has been made in the determination of lactic, acetic - citric, and malic - succinic acids by the titration of their barium salts with 0.05 $\text{N H}_2\text{SO}_4$ in the presence of bromophenol blue, by the addition of ethanol to a concn. of 75 per cent. With 1.5 to 2.5 mg of barium salts in soln. a clear colour change is obtained.

C. D. KOPKIN

2770. A note on the determination of some alkali salts of organic acids by ion exchange. S. M. Blaug (Coll. Pharmacy, State Univ. of Iowa, Iowa City, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, 45 (4), 274-275.—Sodium citrate, lactate and salicylate can be rapidly determined by the use of a cation-exchange resin, followed by titration of the liberated acids with standard alkali. Dextrose does not interfere. The method has been applied to four parenteral solutions of the U.S.P. XV with an accuracy equal to that of the official method. *Procedure*—Pass an aq. soln. (10 ml, containing ≈ 0.5 milli-equiv. of the salt) through a column of Amberlite IR-120 (10 g). Elute with H_2O (4 \times 10 ml), or with 75 per cent. ethanol for salicylate, and titrate with 0.1 N NaOH .

A. R. ROGERS

2771. Direct photometry of colour reactions of sugars on paper. H. Wöhlisch (Physiol.-chem. Inst., University of the Saar, Homburg). *Z. anal. Chem.*, 1956, 150 (1), 2-7.—Paper chromatograms of sugars are quant. evaluated by colour formation with triphenyltetrazolium chloride, benzidine or molybdophosphoric acid, and measurement of the colour of the spot on the paper with a Pulfrich photometer. The cut strip of paper carrying the coloured spot is pressed on to the cell holder and inserted symmetrically into the beam of incident light. The extinction is read against a blank, the appropriate filter being used; in general, log concn. is proportional to extinction. The coloured spot may fit the opening (3 sq. cm) of the cell holder or have a smaller area. For spots of larger area a correction factor must be used. The method is applicable to non-circular spots, and preferably for 3 to 25 μg of sugar.

J. P. STERN

2772. Detection and paper chromatography of sugars and sugar phosphates in picric acid system. H. S. Loring, L. W. Levy and L. K. Moss (Stanford Univ., Stanford, Calif., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part I), 539-540.—The use of the *tert*-butyl alcohol - picric acid - water (80:4:20) solvent system for the paper chromatography of sugar phosphates (*cf. Hanes and Isherwood, Nature*, 1949, 164, 1107) has been extended to the separation of the sugars themselves. Sugars and sugar phosphates are readily detected on the chromatograms by spraying with ethanolic NaOH and heating; they appear as red - brown spots against a yellow background. Values of R_F and of the ratio of the R_F for the compound to that for *D*-ribose are listed for 14 sugars and 6 sugar phosphates.

A. R. ROGERS

2773. Paper chromatography of sugar mixtures on fibre-glass paper. G. Jayme and H. Knolle (Inst. für Cellulosechemie, Darmstadt, Germany). *Angew. Chem.*, 1956, 68 (7), 243-246.—The chromatography of sugar mixtures with butanol - acetone - water (4:5:1) as solvent on fibre-glass in place of cellulose paper is described. The method avoids the adsorption effects that occur when cellulose is used and gives good results provided that impregnation with 0.1 M phosphate buffer (pH 5.0) is carried out before chromatography. Impregnation of cellulose paper with the phosphate also gave sharper separation. It was not found possible to separate mannose, arabinose and fructose, or xylobiose and glucose on fibre-glass.

H. F. W. KIRKPATRICK

2774. Reagent for differentiation of 1:4- and 1:6-linked glucosaccharides. S. Schwimmer and A. Bevenue (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Science*, 1956, 123, 543-544.—Variations in the colour of oligosaccharide spots on paper chromatograms treated with the reagent of Buchan and Savage (*Analyst*, 1952, 77, 401) were found to be due to differences in linkage. Aniline (4 ml) and diphenylamine (4 g) were dissolved separately in acetone and each soln. was made up to 100 ml; the soln. were mixed with 20 ml of 85 per cent. orthophosphoric acid. The air-dried chromatogram was dipped in this reagent, dried again, and then heated at 80° C for 5 min. Saccharides in which the carbon-4 hydroxyl was combined in glucosyl linkage gave blue to purple colours, whereas those in which this hydroxyl was uncombined gave slate, green or yellow spots according to the concn. per unit area of the chromatogram.

H. F. W. KIRKPATRICK

2775. Colorimetric determination of primary aliphatic amines by copper - salicylaldehyde method. F. E. Critchfield and J. B. Johnson (Carbide and Carbon Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part I), 436-440.—A new method is described for the determination of primary aliphatic amines in the presence of secondary and tertiary amines. The primary amine reacts with an aq. reagent containing CuCl_2 , salicylaldehyde and triethanolamine; the complex is extracted into *n*-hexanol, and the Cu in the hexanol layer is determined absorptometrically by reaction with di-(2-hydroxyethyl)dithiocarbamic acid. The accuracy is within 5 per cent. Aromatic amines, polyamines and primary amines branched in the 2-position do not react quant. Strong oxidants or reductants and large amounts of secondary and tertiary amines must be absent. *Procedure*—To the sample (containing ≈ 0.5 mg of primary amine

and >0.01 mg of NH_3) add 2 ml of an aq. soln. containing redistilled triethanolamine (15 per cent.), salicylaldehyde (0.5 per cent.) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.25 per cent.), dilute to 10 ml with H_2O and mix. After 60 min., dilute with *n*-hexanol to 25 ml and shake 15 or 20 times. Mix 5 ml of the *n*-hexanol layer with a mixture of 2 per cent. v/v CS_2 in methanol (2.5 ml) and 5 per cent. diethanolamine in methanol (2.5 ml), dilute to 25 ml with methanol, mix and measure the extinction at 430 $\text{m}\mu$ in 1-cm cells against a similarly treated blank.

A. R. ROGERS

2776. Reaction of carbon disulphide with primary and secondary aliphatic amines as an analytical tool. F. E. Critchfield and J. B. Johnson (Carbide and Carbon Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 430-436.—Primary and secondary amines react with CS_2 to give substituted dithiocarbamic acids, which may be titrated with aq. NaOH. This has been used as the basis of several analytical methods. The accuracies are within ± 0.1 per cent. **Primary and secondary aliphatic amines**—Three solvents are listed—(a) pyridine (50 ml) - isopropyl alcohol (50 ml) - H_2O (25 ml) for amines that give reaction products insol. in isopropyl alcohol; (b) isopropyl alcohol (75 ml) for amines that give sol. reaction products; (c) isopropyl alcohol (75 ml) - pyridine (25 ml) for unreactive amines. Neutralise the sample soln. (containing <15 milli-equiv. of amines) to thymolphthalein with 0.5 *N* HCl or NaOH. Cool to $<0^\circ\text{C}$ (or -10°C if >2 milli-equiv. of NH_3 are present), add CS_2 (5 ml) and titrate with 0.5 *N* NaOH to the first blue or blue - green colour stable for 1 min. Perform a blank titration. Tertiary amines and NH_3 do not interfere. Aromatic amines and aliphatic amines highly branched in the 2-position do not react quantitatively. **Differential determination of primary and secondary aliphatic amines**—Mix the sample (containing <13 milli-equiv. of secondary amine) with a 50 per cent. soln. of 2-ethylhexaldehyde in pyridine (10 ml) containing 0.5 per cent. of phenyl-1-naphthylamine as antioxidant. After 5 min., add the appropriate solvent and cool to -10°C . Add CS_2 (5 ml) and a 1 per cent. soln. of phenolphthalein in pyridine (5 or 6 drops) and immediately titrate with 0.5 *N* NaOH at 0°C to the first pink colour stable for 1 min. Perform a blank titration. Primary alcohol amines, aromatic amines, primary amines highly branched in the 2-position and polyamines do not react quant. with 2-ethylhexaldehyde and interfere. The content of NH_3 plus tertiary amines must be <30 milli-equiv., and of primary amines <16 milli-equiv. **Differential determination of carboxylic acids and anhydrides**—Mix the sample (containing 2 to 3.5 milli-equiv. of acid plus anhydride) with a 0.2 *N* soln. of morpholine in methyl cyanide (25 ml). After 15 min., add isopropyl alcohol (75 ml) and a 1 per cent. soln. of thymolphthalein in pyridine (5 or 6 drops) and titrate with 0.1 *N* NaOH to the first blue colour stable for 15 sec. Add H_2O (20 ml) and CS_2 (5 ml) and titrate the acid derived from the excess of morpholine with 0.1 *N* NaOH to the first blue or blue - green colour stable for 1 min. Perform a blank titration. Acrylic and chloroacetic anhydrides cannot be determined by this method.

A. R. ROGERS

2777. Some colour tests for quinones. H. Karius and G. E. Mapstone (Bituminous Binder Research Unit, Pretoria, S. Africa). *Chem. & Ind.*, 1956,

(15), 266-267.—Colour reactions of a number of quinones with indole, pyrrole and ethylenediamine, respectively, are described. **Procedure**—(a) Five drops of conc. HCl are added to a mixture of 1.0 ml of a 0.5 per cent. ethanolic soln. of indole (or pyrrole) and 2.0 ml of the quinone soln. A colour (usually violet) indicates a quinone. (b) Three drops of ethylenediamine are added to 2 ml of an aq. quinone soln. or 1 ml is added to 3 ml of a light-petroleum soln. Various colours are obtained. The method is applicable to spot tests. 2-Aminoanthraquinone and 1:5-diaminoanthraquinone give no colour with these reagents. Colours and sensitivities are recorded. E. J. H. BIRCH

2778. Micro-determination of luminol by means of chemiluminescence measurement. Sôchirô Musha and Mitsuo Ito (Faculty of Eng., Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 114-118.—The chemiluminescence of luminol (I), brought about by a catalytic oxidation with H_2O_2 in a basic soln., was studied for its application to the photometric analysis of I. The intensity of the luminescence spectrum is so small that a new, sensitive apparatus with a photomultiplier tube was designed for its measurement. When the intensity is plotted against the time of reaction, the total amount of photo-energy (i.e., the area on the diagram) is proportional to the amount of I (2 to 8 mg in 10 ml of 0.6 per cent. Na_2CO_3). Other experimental conditions, including the concn. of H_2O_2 and of the catalyst (Cu^{++}) and the temp., were also studied.

K. SAITO

2779. cycloHexanone. British Standards Institution (Park St., London). B.S. 2711:1956, 8 pp.—Limits are specified for density, boiling range and ash. The material must not be alkaline to phenolphthalein and the acid content must be >0.03 per cent. by wt. as acetic acid. The ketone content must be <88 per cent. as cyclohexanone. Procedures for distillation range, ash determination and determination of acidity are laid down. The ketone content is determined by reaction with hydroxylamine hydrochloride. E. J. H. BIRCH

2780. Assay of refined carbazole. I. Quantitative analysis of refined carbazole by the nitrosation method. Eizo Omori (Fukuyama Dyestuff Plant, Nippon Kayaku Co. Ltd., Fukuyama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 152-154.—Coulson's method for determining carbazole (I) (*Analyst*, 1949, **74**, 46) was examined and slightly modified. The empirical factor of 1.04 is eliminated since it was found that the incompleteness of nitrosation is compensated by other factors, such as a rather high solubility of NO. The purity of NaNO_2 must be determined by the sulphanic acid method and not by its decomposition in acetic acid and chlorobenzene followed by the gasometric determination of NO, which gives a lower value. A smaller reaction vessel (capacity ≈ 85 ml) is recommended.

II. Detection of impurities in refined carbazole. Eizo Omori. *Ibid.*, 1956, **77** (1), 155-159.—The detection and identification of impurities in refined I were studied by various methods, including column chromatography, i.r. and u.v. spectroscopy and polarography. In addition to anthracene (II) (the main impurity), 1:2-, 2:3- and 2:4-benzocarbazole were found in most samples. Since these are nitrosated with the same ease as I, they cause a positive error in the determination of the purity of

I. The difference between the purities as measured by the nitrosation method and the m.p. method can thus be accounted for. Phenanthrene is rarely found in **I**, but its polarographic determination is possible only in the absence of benzocarbazoles.

III. Polarographic determination of anthracene and 2:3-benzocarbazole in refined carbazole. Eizo Omori and Kazuo Fukuda. *Ibid.*, 1956, **77** (1), 159-162.—By using tetramethylammonium bromide (**III**) as supporting electrolyte, polarograms of **II** and 2:3-benzocarbazole (**IV**) were studied in 75 per cent. dioxan containing **I**. The wave heights of **II** ($E_{1/2}$ = 1.98 V vs. the S.C.E.) and **IV** (-2.35 V) are proportional to concn. (<5 per cent. of **II** and <3 per cent. of **IV** in **I**). When both contents are <0.2 per cent., the measurement of wave height is difficult, but this can be overcome by adding a small known amount of **II**. The sample (30 mg) is dissolved in dioxan (3-75 ml) and treated with water (1.25 ml) containing 0.076 g of **III**. This soln. is bubbled with a stream of H and submitted to polarography at $15^\circ \pm 0.5^\circ$ C. The error is ≈ 0.04 per cent. (absolute) for **II** and ≈ 0.02 per cent. for **IV**. K. SAITO

2781. Dipentene. British Standards Institution (Park St., London). B.S. 2712:1956, 9 pp.—Dipentene is specified as consisting essentially of monocyclic terpenes, substantially dipentene; limits are specified for density, boiling range, refractive index and residue on evaporation. The material must not alter the colour of added thymol blue. The matter insol. in H_2SO_4 must be >10 per cent. by vol. The flash point (Abel method) must be $<90^\circ$ F. The content of corrosive sulphur compounds must be low enough to cause no more than a slight discoloration of polished electrolytic copper foil after 2 hr. at $100^\circ \pm 2^\circ$ C. Procedures are also laid down for the determination of the distillation range, and for evaporation under vacuum for the determination of residue. The matter insol. in H_2SO_4 is determined by adding 10 ml of the dipentene dropwise, over 10 min., to 20 ml of at least 98 per cent. H_2SO_4 cooled in ice-water, and then heating to a temp. of 60° to 65° C for 10 min. on a water bath. The vol. undissolved is measured after the cooled mixture has been set aside overnight. E. J. H. BIRCH

2782. Method for the rapid quantitative determination of total pinenes in mixtures of terpenes. I. I. Bardyshev, O. I. Chernyayeva and A. N. Litvinova. *Gidroliznaya i Lesokhim. Prom.*, 1955, (2), 15-17; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,342.—A thermometric method is described, based on the measurement of the temp. of isomerisation, polymerisation and partial etherification reactions of the isomerisation products of α - (**I**) and β -pinenes (**II**) by the action of H_2SO_4 in acetic acid medium. Of the three terpene hydrocarbons of turpentine, only **I** and **II** give a change of temp. under the reaction conditions described. The total amount of heat evolved is proportional to the content of **I** and **II**. The sample soln. (10 ml) and a mixture of 100 per cent. acetic acid and 50 per cent. H_2SO_4 (10:1 by vol.) (10 ml) are mixed in a test-tube in a Dewar flask at $25^\circ \pm 0.1^\circ$ C. The apparatus is kept in a regulated water bath. At first the temp. drops by 0.2° to 0.3° C because of the soln. effect. Increase of temp. of the reaction, Δt , is calculated by subtracting the min. temp. from the max. temp. reached, and then the content of **I** is determined by a calibration curve made from an artificial mixture of pure **I** dissolved in turpentine

(from which **I** and **II** have been completely distilled off). The standard deviation in the determination of Δt is ± 0.13 per cent., equiv. to ± 0.5 per cent. of **I**. The max. temp. is reached for turpentine in 3 to 6 min., and for distilled residues in 30 min. The distilled residues are therefore diluted with pure **I** (1:1 by wt.). The described method gives a provisional content of **I** for turpentine contain **II** also, the Δt of which is higher. To determine the actual content of **I** plus **II**, subtract 1.5 per cent. (experimental correction calculated on a max. content of 8 per cent. of **II** in oil of *Pinus sylvestris*) from the result obtained. Camphene does not interfere. C. D. KOPKIN

2783. Analytical method for thujaplicins. H. MacLean and J. A. F. Gardner (Forest Products Lab. of Canada, Vancouver, B.C., Canada). *Anal. Chem.*, 1956, **28** (4, Part 1), 509-512.—A rapid method is given for the determination of the thujaplicins (isopropyltropolones), based on absorptiometry of their red ferric chelates. The accuracy is ≈ 98 per cent. with coeff. of variation $\approx \pm 1$ per cent. *Procedure*—Extract the sample (2 g in 40-mesh powder) with boiling water (100 ml + 50 ml + 25 ml), cool and dilute the aq. soln. to 200 ml. Extract a 5-ml aliquot with *n*-hexane (2 \times 5 ml). To the combined extracts add $CHCl_3$ (10 ml) and aq. ferric acetate soln. (1 per cent. in Fe) (5 ml). Shake for 5 min., filter and dilute the organic layer to 25 ml with $CHCl_3$. Measure the extinction, with a blue filter (425 $m\mu$) and a hexane- $CHCl_3$ (2:3) blank. Calculate by use of a calibration curve. The absorption spectra of the thujaplicins are not identical, and an estimate of the ratio of the isomers is possible by determining the position of the maximum with a spectrophotometer. A. R. ROGERS

2784. Fluorescence spectra of petroleum oils and their fractions in liquid form and on chromatographic columns. M. L. Kats and N. K. Sidorov. *Uchen. Zap. Saratov. Univ.*, 1954, **40**, 3-59; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,626.—The fluorescence spectrum of crude petroleum in the visible region is characterised by the presence of four maxima at 472 to 476, 505 to 510, 540 to 545 and 620 to 626 $m\mu$. The 472 to 476- $m\mu$ band is due to the fluorescence of oils, the 505 to 510 and 540 to 545- $m\mu$ bands are due to resins, and the 620 to 626- $m\mu$ band is due to asphalts. Fluorescence spectra of different oils do not differ in position and number of bands; the oils are therefore composed of the same fluorescing components. The spectra differ in the relative intensities of the bands for each oil, therefore different oils contain differing proportions of fluorescing substances. The relative intensities of the bands, being connected with the quantitative proportions of fluorescing components in the oil, may serve as a characteristic of the oil. The use of visual ultrachromatographic analysis of the composition of oils and oil products is based on the assumption that the colour of each zone is caused by one fluorescing component. However, the fluorescence spectra studied by the authors show that the zones, as a rule, are due to several components, and this should be remembered when using this method of analysis. C. D. KOPKIN

2785. The use of infra-red spectroscopy in research on oil products. K. I. Zimina, A. V. Jogansen and A. G. Siryuk. *Izv. Akad. Nauk, SSSR, Ser. Fiz.*, 1954, **18** (6), 707; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,201.—Group structural analysis is

used in research on petrol, kerosene, oils and resins. The unsat. hydrocarbon content is established by the bands—(i) $-\text{RCH}:\text{CH}_2$ (909 and 983 cm^{-1}); (ii) $-\text{RR}'\text{C}:\text{CH}_2$ ($\approx 890\text{ cm}^{-1}$); (iii) *trans* $-\text{RCH}:\text{CHR}'$ ($\approx 970\text{ cm}^{-1}$); (iv) $-\text{RR}'\text{C}:\text{CHR}'$ ($\approx 820\text{ cm}^{-1}$). In motor and aviation spirits from catalytic cracking, types (iv) and (ii) predominate, and type (iii) is present; in petrol and kerosene from thermal cracking, all types (i to iv) are present. The band $\delta\text{CH}_3 = 1380\text{ cm}^{-1}$ has shown that isoparaffins are present in normal paraffins produced from kerosene by direct distillation during removal of paraffins by urea, and that, in oil fractions, the increase of branching or number of side-chains in the aromatics is in proportion to the increase in mol. wt. of the fractions. Resins of different oils have qualitatively similar spectra, differing only in intensity of certain bands. C. D. KOPKIN

2786. Total naphthenes in gasoline by refractivity intercept. Analysis of six- to eight-carbon saturates. J. C. S. Wood, A. Sankin and C. C. Martin (Sun Oil Co., Norwood, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 526-530.—The refractivity intercept method is applicable to the determination of naphthenes in the presence of acyclic paraffins after de-aromatization of the sample (cf. *Anal. Chem.*, 1947, **19**, 175). By adjusting the paraffin and naphthene lines for the approximate distribution of the individual hydrocarbons in naturally occurring petroleum, improved refractivity intercept-density charts have been developed for the C_6 to C_8 range. The method is accurate to within ± 2 per cent.

A. R. ROGERS

2787. The analysis of the aromatic portion of lignoin by combined emission spectra. B. A. Kazanskii, G. S. Landeberg, V. T. Aleksanyan, T. F. Bulanova, A. L. Liberman, E. A. Mikhailova, A. F. Plate, Kh. E. Sterin and S. A. Ukholin. *Izv. Akad. Nauk, SSSR, Ser. Fiz.*, 1954, **18** (6), 704-706; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,204.—The analysis of the natural (primary) aromatics of lignoin and the aromatics (secondary) formed from its cyclohexane portion is carried out by the use of the following lines, characteristic of the type of substitution in the benzene nucleus (in cm^{-1} , intensity in brackets)—monoalkylbenzenes 621 ± 2 (40), 1002 ± 2 (350), 1031 ± 1 (75), 1156 ± 1 (30), 1182 ± 1 (15), 1205 ± 5 (65); 1:2-dialkylbenzenes 586 ± 4 (35), 714 ± 3 (130), 1039 ± 6 (200), 1220 ± 5 (150); 1:3-dialkylbenzenes 525 ± 6 (80), 716 ± 8 (140), 1002 ± 1 (400), 1247 ± 3 (65); 1:4-dialkylbenzenes 642 ± 2 (50), $780-810$ (250), 1204 ± 4 (100); 1:2:3-trialkylbenzenes 482 ± 2 (75), 532 ± 3 (55), 652 ± 3 (450), 994 ± 1 (50), 1097 ± 5 (100); 1:2:4-trialkylbenzenes 458 to 485 (75), 548 ± 6 (120), 738 ± 5 (150), 1245 ± 2 (120); 1:3:5-trialkylbenzenes 513 ± 2 (120), 574 ± 3 (240), 999 ± 2 (350), 1297 ± 3 (100); naphthalene and its homologues 510 to 525 (≈ 250), 1368 to 1385 (≈ 2500), 1570 to 1585 (300 to 500); diphenyl homologues 1270 to 1285 . The results of narrow-group and individual analyses do not greatly differ.

C. D. KOPKIN

2788. Determination of tetraethyl-lead in petrol by X-ray absorption. A. Ferro and C. P. Galotto (Lab. Fiat, Torino, Italy). *Ann. Chim., Roma*, 1955, **45** (12), 1234-1243.—The method consists in measuring the absorption increment corresponding to the sublevel L_{111} of the tetraethyl-lead present in the petrol. An apparatus of the General Electric

type XRD3 is used with anti-cathode tube of Mo (18 kV). The emitted radiation, rendered monochromatic by a crystal of NaCl, is passed through the cell containing the petrol under test and its intensity is measured for various angular positions with a Geiger counter connected to a scaler.

L. A. O'NEILL

2789. Determination of six- and seven-carbon naphthenes in catalytic reforming feed. C. C. Martin, S. S. Kurtz, jun., G. R. Bond, J. A. Grant, R. Griffith, C. E. Headington, B. J. Heinrich, C. W. Key, G. R. Lake, R. L. LeTourneau, D. R. Long, A. A. Rawlings and E. B. Tucker (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 490-494.—This is a report of the sub-committee on the determination of naphthenic hydrocarbons of the Committee on Analytical Research of the Division of Refining of the American Petroleum Institute. Co-operative work in 12 laboratories has shown that several methods give accurate analyses of C_6 and C_7 naphthenes in reformer charges. Preliminary fractional distillation is desirable with all methods. Mass spectrometry is the most rapid method; i.r. spectrometry is the best method for complete analysis, but preliminary removal of aromatics is desirable. "Short-cut" methods, such as the use of refractivity intercept charts or analytical dehydrogenation, also give good results. In one sample, cyclohexane and methylcyclopentane have been determined with a coefficient of variation of 0.5 per cent., and methylcyclohexane and the sum of the cyclopentane derivatives with slightly less precision.

A. R. ROGERS

2790. Nephelometric determination of sodium carboxymethylcellulose in fibrous material based on cellulose. E. Wurz (Lab. der Zellulosefabr. A.-G., Leoben, Austria). *Öst. ChemZtg.*, 1955, **56** (10), 285-286.—Various methods for the estimation of Na carboxymethylcellulose (I) in fibres derived from cellulose are reviewed and an analytical process is described by means of which the retention of I in paper and the effect of sizing and desizing agents in textiles (cotton, cellulose-wool, etc.) can be evaluated. A 1-g sample of the test material (of known moisture content) is cut into flocks ($\approx 0.5\text{ cm sq.}$) and immersed in 25 to 100 ml of 60 per cent. NaOH (according to the expected content of I). After 1 hr. swelling, the suspension is filtered through sintered glass and 10 ml of clear filtrate are treated with 1 ml of Zephrol (a mixture of alkylbenzyltrimethylammonium chlorides). The light absorption of the resulting turbid soln. is measured in a Lange colorimeter and results are calculated with the aid of graduated control soln., containing the same fibrous material without I. Technological applications of this new method in the paper and textile industries are discussed.

S.C.I. ABSTR.

2791. The determination of oleic acid and potassium oleate in [solutions in] white spirit. S. C. Mitchell and E. J. Davies (Dyers and Cleaners Res. Org., 4 Lifton Place, Leeds, England). *Analyt.*, 1956, **81**, 121-122.—In the method proposed, 0.1 N KOH soln. is prepared in 20 ml of water, 60 ml of ethanediol, 520 ml of isopropyl alcohol and 400 ml of white spirit. A procedure for the standardisation of this soln. against benzoic acid is described. The acid titrant is 0.1 N HClO_4 in isopropyl alcohol and white spirit (3:2) standardised against the KOH soln. Suitable aliquots of the dry-cleaning soap in white spirit are diluted with

neutral isopropyl alcohol; one is titrated for free fatty acid with the standard KOH soln. to the phenolphthalein end-point and the other for total fatty acid with the HClO_4 soln. to the red end-point of thymol blue. When applied to the determination of the equiv. wt. of oleic acid (282), the method gave low results (278.4) and hence tends to give high results in the determination of free fatty acids. When known materials are used the oleic acid equiv. of the standard KOH should be determined. The method is not affected by the presence of auxiliary solvents, e.g., alcohols, Cellosolves and Carbitols.

A. O. JONES

2792. Determination of quaternary ammonium compounds as tungstophosphates. P. A. Lincoln and C. C. T. Chinnick [Milton Industrial Chemicals (London) Ltd., 42 Weymouth St., London]. *Analyst*, 1956, **81**, 100-104.—Surface-active quaternary ammonium compounds are quant. pptd. by tungstophosphoric acid (I). The sample (≈ 0.0002 to 0.0006 g of the quaternary compound), in acidified aq. soln. containing NaCl, is treated at boiling point with 10 per cent. I soln. and the mixture is boiled to coagulate the ppt., then cooled. The ppt. is collected in a tared No. 3 sintered porcelain crucible, washed with water, dried at 105°C to constant wt. and finally ignited at dull-red heat and re-weighed. If the quaternary compound is represented by QX (X being usually a halide ion) the dried ppt. is $\text{Q}_3\text{PO}_4 \cdot 12\text{WO}_3$ and the residue after ignition is $\text{HPO}_4 \cdot 12\text{WO}_3$. These reactions provide enough data for the determination of the quaternary compound present whether or not its mol. wt. is known. Also the mol. wt. of an unknown compound may be calculated. The sample must be free from NH_3 and amines. These can be removed by dissolving the sample in isoamyl alcohol and washing the soln. with N HCl . The soln. in isoamyl alcohol is then diluted with water and treated with I.

A. O. JONES

2793. Thymol blue as reagent for anion-active colloidal electrolytes. K. Peter. *Fette u. Seifen*, 1954, **56** (12), 997-1001.—A systematic process of qual. analysis is described by which anion-active colloidal electrolytes are identified with thymol blue. The method is based on the selective adsorption properties of various capillary-active compounds (X) which cause characteristic changes in the transition range of this indicator. (a) A 1 per cent. soln. of neutral X is prepared from an alcoholic extract of the test mixture (preparation given) and 5 ml of the soln. are added to 5 ml of 0.005 N HCl , containing 3 drops of 0.1 per cent. aq. thymol blue. A purple coloration indicates the presence of 15 specified compounds (fatty acid monoglyceride sulphates, sulphosuccinic esters, alkylbenzenesulphonates, etc.). Sulphated fatty acids, alkylbenzimidazolesulphonates, condensation products of fatty acids with aminoalkylcarboxylic acids, or with protein degradation products give no coloration. (b) When this test is repeated with diluted (0.1 per cent.) X, a negative result excludes four of the compounds listed under (a). (c) Group identification is made by the use of HCl - Na citrate buffer soln. in place of the dil. HCl in test (a). Colours are then given at the pH value shown—monolaurin sulphate, 2.6 to 2.8; dioctyl sulphosuccinate, 2.7 to 2.9; dodecyl benzenesulphonate, 3.4 to 3.6. (d) A scheme for separating and identifying sulphonates in fatty alcohol sulphates, listed under (a), is presented.

S.C.I. ABSTR.

2794. Modified apparatus for estimation of volatile oils. R. N. Chakravarti, S. Dash and A. B. Datta (Dept. of Chem., Sch. Tropical Medicine, Calcutta). *J. Inst. Chem., India*, 1955, **27** (4), 266-273.—The apparatus recommended in the 1953 B.P. is modified by the introduction of a wide cylindrical portion between the condenser and the graduated tube and a wide-bore stopcock in the inclined arm joining the bottom of the graduated tube to the still-head. For the estimation of volatile oils lighter than water, the stopcock is kept open and the apparatus is used as described in the B.P. Oils heavier than water are collected in the wide cylindrical portion and from a pellicle on top of the water, excess of which is removed by intermittently opening and closing the stopcock. Oils that tend to solidify are distilled together with a small quantity of xylene to maintain the distillate liquid.

J. M. JACOBS

2795. Simplified method for the analysis of alkylid resins. A. Davidsohn. *Paint Tech.*, 1955, **19**, 301.—For the fatty acids (including any rosin acids present), 3 to 5 g of the alkylid are saponified with 150 ml of 0.5 N alcoholic KOH, the product is diluted with 150 ml of water, and 5 to 10 per cent. HCl is added until the solution is just acid to methyl red. The fatty and rosin acids are extracted with light petroleum, the solution is evaporated, and the residue is weighed to give the percentage of fatty acids (c), the acid value (b) of which is then determined. When hydroxylated fatty acids are present, as in blown- or castor-oil alkylids, the alcohol must be evaporated off after the saponification, and ether used for extracting the fatty acids. The saponification value (a) of the alkylid is finally determined and the percentage of phthalic acid (assuming that there are no other dibasic acids present) is $100(a - bc/100)/757$.

D. R. DUNCAN

2796. Infra-red spectroscopy in the quantitative analysis of paint and varnish materials. N. M. Peacock and A. W. Pross. *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1955, **27**, 702-707.—Some typical applications are described. Long-oil and short-oil alkylids may be differentiated by comparison of the extinctions at 1725 cm^{-1} (C:O) or 2940 cm^{-1} (C:H). Urea-alkylid mixtures of different composition may be studied by comparing the 1725 cm^{-1} band with that at 1650 cm^{-1} due to the urea resin. An approximation of the oil length of epoxy esters can be derived from the 1725 cm^{-1} band.

L. A. O'NEILL

2797. Determination of lead cyanamide. E. Cianetti (Inst. Mercologia, Rome University). *Olii Min.*, 1955, **32** (12), 275-276.—A modified Kjeldahl method for the determination of PbCN_2 , used for colouring varnishes, is described. A mixture of H_3PO_4 and H_2SO_4 is used for digesting the specimen (previously dried to constant weight at 100° to 105°C), after which the usual Kjeldahl method is followed. By this procedure commercial PbCN_2 is shown to be ≈ 98 per cent. pure. An accuracy within $\approx \pm 0.2$ per cent. is attained.

C. A. FINCH

2798. Semi-micro determination of nitrogen in coal. J. A. Corrales Zarauza (Inst. Nacional del Carbón, Oviedo). *Bol. Inst. Nac. Carbón*, 1955, **4** (24), 306-311.—The I.S.O. modification of the Kjeldahl method, in which a Hg - Se catalyst is used (I.S.O./TC27, 1954, 222E) has been compared on the semi-micro scale for the determination of N in

Spanish coals with the Lange - Winzen modification, in which MnO_2 is used with the Hg - Se as catalyst. A macro-Kjeldahl method is used as reference. The modification with MnO_2 was found to give irregular and low results; if lower proportions of MnO_2 than suggested were used and a longer time of digestion were allowed, the results were consistent, but still low. In this modification, H_2S was often detected in the distillate. On the other hand the I.S.O. modification gave results in agreement with the macro-method, provided the time of distillation (which depends on the type of apparatus and should not be rigidly defined) was extended.

L. A. O'NEILL

2799. Statistical study of tannin analysis and sampling. R. C. Putnam, C. B. Crandall and E. Facer (U.S. Testing Co. Inc., Hoboken, N.J., U.S.A.). *J. Amer. Leath. Chem. Ass.*, 1955, **50** (11), 534-546.—A series of quebracho tannin shipments were sampled and analysed, duplicate samples being taken in each batch. After consideration of results from these tests a schedule for sampling has been designed which allows for the size of the batch, and is considered to be an improvement on the present method of the American Leather Chemists' Association. Data for use in preparing control charts are given and compared with A.L.C.A. "good agreement" values.

B. R. HAZEL

2800. Report of the committee for determination of copper in vegetable tanning extracts. Society of Leather Trades' Chemists ("Craigieburn," Duppas Hill Rd., Croydon, England). *J. Soc. Leath. Tr. Chem.*, 1955, **39** (12), 374-376.—In the colorimetric method described, a Cu complex is formed with Na diethyldithiocarbamate. Tetrasodium pyrophosphate is added to sequester Mg, Mn and Ca, and to overcome opalescence. Results are reproducible and agree with those from electrolytic methods.

B. R. HAZEL

See also Abstracts 2814, 2891.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2801. The blood ammonia in normal persons. W. G. Calkins (Univ. Kansas Med. Centre, Kansas City, U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (3), 343-348.—Conway's microdiffusion technique is adapted for the determination of concn. of NH_4^+ in blood. *Procedure*—Place 1 ml of 0.0002 N HCl containing methyl red - methylene blue indicator in the inner chamber of a diffusion dish, and 1 ml of NH_3 -free aq. satd. K_2CO_3 in the outer chamber. Introduce 1 ml of the oxalated blood sample from the tuberculin syringe in which the sample was drawn into the outer chamber. Immediately place the cover in position, mix the contents of the outer chamber by swirling and allow diffusion to take place for 15 min. at room temp. Titrate the contents of the inner chamber with 0.0005 N $\text{Ba}(\text{OH})_2$. Carry out a blank and a standard determination with aq. $(\text{NH}_4)_2\text{SO}_4$ (100 μg of ammonia nitrogen per 100 ml) at the same time. The error on standard blood samples is 10 per cent. Fasting blood levels in 100 normal persons were 34 to 133 μg of ammonia nitrogen per 100 ml (average 79.5, standard deviation 2.68). W. H. C. SHAW

2802. Improved micro-manometric methods for the analysis of respiratory gases in plasma and whole blood. D. A. Holaday and M. Verosky (Columbia Univ., New York, N.Y., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (4), 634-644.—Methods which require 0.03 ml of sample are detailed for the determination of CO_2 in plasma and of O and CO_2 in whole blood. The apparatus required, sources of error and the corrections necessary to obtain accurate results on whole blood are discussed. Results given by the proposed methods agree well with those obtained by the standard Van Slyke - Neill procedure (*J. Biol. Chem.*, 1925, **61**, 523).

W. H. C. SHAW

2803. Evaluation of a rapid micro-method for the determination of serum calcium. H. C. Leifheit (New England Med. Center, Boston, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (4), 623-633.—Total Ca and Mg are determined on 0.1 ml of serum by a simple method requiring titration with standardised EDTA (disodium salt) solution in the presence of ethanolamine buffer, and with Eriochrome black T as indicator. The amount of Mg is determined separately, after pptn. of Ca as oxalate, by a modification of the Titan yellow method, and the Mg found is deducted from the total. Alternatively, but less accurately, the mean Mg content of human serum (1.64 milli-equiv. per litre) may be deducted. Results for Ca by the proposed method show good agreement with those given by a standard oxalate - KMnO_4 titration procedure at both normal and abnormal serum-calcium levels.

W. H. C. SHAW

2804. Determination of calcium, magnesium, zinc and iron in animal tissue. R. Hamm (Inst. Bundesforsch. f. Fleischwirtschaft, Kulmbach, Germany). *Mikrochim. Acta*, 1956, (1-3), 268-272.—A method is described for determining Ca, Mg, Zn and Fe on 1 to 5 g of tissue. Ash at 550°C in a platinum dish. Dissolve the ash in 0.1 N HCl. Pass the soln. through a cation-exchange column packed with 1 to 1.5 g of Lewatit S100. Wash the column with water. The washings contain the phosphate and 90 to 95 per cent. of the Fe, whilst Ca, Mg, Zn and the remainder of the Fe are retained on the column. Elute the column with 5 N HCl and in one aliquot of the eluate determine Ca by titration with EDTA (disodium salt), with murexide as indicator. Evaporate a further aliquot to dryness; take up in 0.1 N HCl; titrate with EDTA (disodium salt) to Eriochrome black T in the presence of KCN to determine Ca plus Mg, and after addition of chloral hydrate ascertain the Zn by compleximetric titration. Combine an aliquot from the eluate and the water washings and determine Fe by the o-phenanthroline reaction. The mean error claimed for Ca, Mg and Fe is ± 1.5 per cent., and for Zn ± 2.6 per cent. A complete analysis requires half a day. D. F. PHILLIPS

2805. The spectrometric determination of copper in serum. I. Ružđić and K. Blažević (Centr. Med.-chem. Lab., Zagreb, Yugoslavia). *Mikrochim. Acta*, 1956, (1-3), 288-298.—A direct and rapid method, with pectin as a protective colloid, for stabilising the colour of the copper diethyldithiocarbamate complex is described. *Procedure*—Mix 2 ml of serum with 6 ml of H_2O in a centrifuge tube and centrifuge with 2 ml of 20 per cent. trichloroacetic acid. Place the tube in a water bath at 90° to 95°C for 10 min. Cool to room temperature and filter. Transfer 5 ml of clear filtrate to a test glass

calibrated at 15 ml. Add 1 ml of a satd. soln. of sodium pyrophosphate, 2 ml of aq. NH_3 , 1 ml of 0.05 per cent. pectin soln. and 1 ml of 0.2 per cent. Na diethyldithiocarbamate, and dilute to the mark with H_2O . Measure the extinction in a Zeiss spectrophotometer at 440 μ in a 3-cm cell. An adaptation of the method for a 1-ml sample of serum is also described. Stringent precautions against contamination of Cu from reagents and glassware are essential. Statistical treatment of results obtained shows that whilst the extinction values observed in aqueous and serum soln. are significantly different, the differences are unimportant. The lower limit of determination of Cu is 2.5 μg per ml, with an error up to 4 per cent. of the content at 99.9 per cent. confidence limits.

D. F. PHILLIPS

2806. A spectrochemical micro-determination of lead in biological material. K. Pfeilsticker (Chem. Untersuch. Stuttgart, Germany). *Mikrochim. Acta*, 1956, (1-3), 319-333.—Full details are given of simple procedures for accumulating Pb together with other heavy elements in the ash of biological materials. Sample quantities are—for blood, 2 ml, and for urine, 30 ml; solid samples vary from 0.1 g for bone to 1 g for organs. Initially 8 μg of In are added as internal standard. The entire preparation is conducted in a 10-ml (30 ml for urine) quartz or platinum dish. The final concentrate is mixed with a bonding soln. and mounted on aluminium electrodes of 99.998 per cent. purity. A medium dispersion spectrograph (Zeiss Q24) is used with excitation by an interrupted a.c. arc. Under these conditions complete consumption of the sample occurs with a 15-sec. exposure. Selected lines are Pb 4057.8 \AA with In 3258.6 \AA . The limit of detection is 0.2 μg of Pb present on the electrodes. With duplicate exposures a coeff. of variation of ± 5.4 per cent. is claimed. Satisfactory agreement with the dithizone and polarographic methods is shown. One analyst can complete 16 samples in a day. By introduction of Pd and Ga as additional internal standards simultaneous determination of Mn, Cu, Zn, Cd and Cr can be made from the same exposure. Precautions against extraneous contamination from Pb are discussed. Normal blood is found to contain 20 to 40 μg of Pb per 100 ml, rising to 70 μg when poisoning becomes evident, and as much as 300 μg in bad cases.

D. F. PHILLIPS

2807. Methods of blood-iodine determination. H. Spitzzy and H. Lieb (Paracelsus Inst., Bad Hall, Upper Austria). *Mikrochim. Acta*, 1956, (1-3), 273-287.—The authors briefly review the various methods which have been published since 1926 for determining iodine in biological materials. For the determination of blood iodine and its fractions, the method of Klein (*Biochem. Z.*, 1952, 322, 388) was selected as most promising for investigation. The various stages of this method were followed with ^{131}I . By this means it was shown that only 79 per cent. of the I known to be present was recovered after 15 min. distillation, but this is increased to ≈ 90 per cent. by increasing the vol. of distillate collected by stronger heating. The addition of various materials suggested in the literature as suitable reducing agents to be included in the alkaline receiving liquid was shown to have no effect. No increase in recovery was shown by the addition of H_2O_2 as suggested by Moran, although it prevented the passing over of substances which upset the iodine catalysis reaction. The addition of H_2O_2 was also shown to render unneces-

sary the presence of organic carrier materials in substances of high water content, if added directly after reduction of the iodic acid. Ashing temperatures up to 250°C caused no loss of I, despite statements to the contrary by other writers. With highly purified reagents (Merck) blank values of approx. 0.036 μg of I were obtained. It is concluded that the direct methods of Klein (*Biochem. Z.*, 1954, 326, 9) for the determination of inorganic and organic-bound I in serum are practicable.

D. F. PHILLIPS

2808. The determination of serum bicarbonate by flame photometry. S. Davis and J. H. Simpson, jun. (Veterans Admin. Hosp., Indianapolis, Ind., U.S.A.). *J. Biol. Chem.*, 1956, 219 (2), 885-892.—A flame-photometric method is described for the determination of serum bicarbonate. It is a modification of that of Sobel and Eichen (*Brit. Abstr. C*, 1953, 71) and depends on flame-photometric analyses of the BaCO_3 precipitate. The method gives values for serum bicarbonate which vary from 96.0 to 103.4 per cent. of the values obtained by the Van Slyke method.

J. N. ASHLEY

2809. Internal electrolysis as an analytical method for the determination of small quantities of certain elements. I. G. Druzhinin and P. S. Kisilitsyn. *Trudy Inst. Khim. Akad. Nauk Kirghiz SSR*, 1955, (6), 139-145; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,464.—Possibilities are indicated of the use of internal electrolysis for the determination of metals in samples of biological origin in toxicological studies. Internal electrolysis can separate almost completely Ag, Cu, Bi and Hg in a sulphate soln. obtained after decomposition of the sample in HNO_3 - H_2SO_4 . The four elements can be quantitatively determined with satisfactory accuracy in about 1 hr. The use of a graphite electrode for the separation instead of the expensive platinum electrode is sometimes possible.

C. D. KOPKIN

2810. Determination of catecholamines and catechols in human urine. M. Goldstein and I. Abelin (Med.-chem. Inst. Univ. Berne). *Helv. Chim. Acta*, 1956, 39 (1), 158-167.—A paper-chromatographic method is used for the determination of adrenaline, noradrenaline and hydroxytyramine in human urine. A detailed isolation procedure is given, followed by a method for their chromatographic separation. Quant. fluorimetric determination is also employed.

C. A. FINCH

2811. A rapid ultra-violet spectrophotometric method for the detection, estimation and identification of barbiturates in biological material. P. M. G. Broughton (Dept. of Clin. Biochem., Radcliffe Infirmary, Oxford). *Biochem. J.*, 1956, 63 (2), 207-213.—The method described is based on that of Goldbaum (*Anal. Chem.*, 1952, 24, 1604). Characteristic absorption spectra of barbiturates in various concentrations are given and the criteria for their detection are enumerated. Absorption spectra of salicylic acid and sulphonamides, which can interfere with the determination, are given and the recognition or removal of these compounds is described. Bemegride (β -ethyl- β -methylglutamide) interferes in the detection of barbiturates by the described method, and also with the reaction between barbiturates and Co^{++} . A method is described for the partial identification of barbiturates by measurement of the amount remaining after alkaline hydrolysis under standard conditions. Spectrophotometric measurement is made before

and after heating the sample with 0.45 N NaOH in a boiling-water bath for 15 min. J. N. ASHLEY

2812. A method for the simultaneous determination of phenobarbitone and diphenylhydantoin in blood. G. L. Plaa and C. H. Hine (Med. Sch., California Univ., San Francisco, U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (4), 649-657.—In the simple rapid method described, diphenylhydantoin (I) is separated from phenobarbitone (II) by preliminary extraction of whole oxalated blood (5 ml), adjusted to pH 8.5 (NaOH and NaHCO_3), with a mixture of cyclohexane and *n*-butanol (20:1). After separating the solvent and washing with N HCl, I is re-extracted into NaOH- NaHCO_3 buffer (pH 11) and extinctions are measured at 260, 250, 240 and 235 m μ . The difference in extinctions at these wavelengths when the pH is adjusted to 12.5 with NaOH is a measure of the I present. The blood sample remaining is then adjusted to a pH of 5.5 to 6.0 with acetic acid. II is extracted into CHCl_3 , and is then separated and washed with 10 N H_2SO_4 , and the II is re-extracted into 0.3 N NaOH. The extinction of the NaOH solution at 260, 250 and 240 m μ is measured, the pH is adjusted to between 10 and 10.5 with saturated aq. KHCO_3 , and the change in extinction is used for calculating II. The method is highly specific and suitable for clinical and toxicological purposes.

W. H. C. SHAW

2813. Studies on the biosynthesis of blood pigments. II. Haem and porphyrin formation in intact chicken erythrocytes. [Determination of porphyrins.] E. I. B. Dresel and J. E. Falk (Univ. Coll. Hosp. Med. Sch., London). *Biochem. J.*, 1956, **63** (1), 72-79.—Methods are described for the determination of haem, proto-, copro-, and uroporphyrin formed in intact chicken erythrocytes after incubation with glycine, δ -aminolaevulinic acid, or porphobilinogen. Haem is determined, after separation from porphyrins, by conversion into the copper complex of protoporphyrin dimethyl ester, the radioactivity of which is determined after radioactive glycine has been used. The other porphyrins are determined spectrophotometrically.

J. N. ASHLEY

2814. Gas-liquid chromatography: the separation and identification of the methyl esters of saturated and unsaturated acids from formic acid to *n*-octadecanoic acid. A. T. James and A. J. P. Martin (Nat. Inst. for Med. Res., Mill Hill, London). *Biochem. J.*, 1956, **63** (1), 144-152.—Micro amounts of the methyl esters of C_1 to C_{18} saturated fatty acids are separated at 78.7° and 100° C by gas-liquid chromatography, and esters of the saturated and unsaturated C_8 to C_{18} acids are separated at 197° C. There is good separation of *n*- and *iso*- or *anteiso*-saturated acids, and mono- and di-unsaturated acids are separated from the corresponding saturated acids on 4-ft. columns. Methods are described for distinguishing between saturated and unsaturated acids by chromatographic behaviour before and after chemical modification.

J. N. ASHLEY

2815. A colorimetric method for the determination of certain keto acids. M. W. Slein and G. F. Logan (Camp Detrick, Frederick, Md., U.S.A.). *Biochim. Biophys. Acta*, 1956, **20** (1), 118-128.—Greater sensitivity is obtained in the hydroxylamine- FeCl_3 method of Lipmann and Tuttle (*J. Biol. Chem.*, 1945, **159**, 21) by decreasing the acidity during colour development with FeCl_3 . The effects

of pH and concn. of FeCl_3 and hydroxylamine are investigated; the behaviour of different keto acids and of hydroxy acids, aldehydes and phenols in the reaction is studied, and the specificity of the method is discussed.

W. H. C. SHAW

2816. Analysis of radioactive phosphates in extracts of cerebral tissues. P. J. Heald (Inst. of Psychiatry, Maudsley Hosp., London). *Biochem. J.*, 1956, **63** (2), 235-242.—The system of analysis described for the acid-soluble phosphates present in cerebral tissues is based on a paper-electrophoretic method and can be used in the study of the metabolism of ^{32}P . Trichloroacetic acid extracts of the tissue are fractionated into groups by pptn. as barium salts, which are then decomposed by a cation-exchange resin. The resulting solution is freeze-dried and the phosphates are then separated by paper electrophoresis. After elution of the various fractions, the P is determined by standard procedures. The method is useful for the fractionation of small amounts of phosphates (120 to 130 μg of total P), and is specific for adenosine triphosphate, inorganic phosphate and creatine phosphate.

J. N. ASHLEY

2817. Determination of phosphocreatine and other phosphorylated intermediates with Dowex-1 resin. L. G. Aboud (Div. of Psychiatry, Univ. of Illinois College of Medicine, Chicago, U.S.A.). *Science*, 1956, **123**, 545-546.—The use of 100 to 200-mesh Dowex-1 X8 resin with elution at 0° C prevents the hydrolysis of labile phosphates that occurs with finer mesh resins. The resin (stored in conc. formic acid) was washed in columns (6 cm \times 0.7 cm) with 10 vol. of conc. formic acid and then with water until neutral. The neutralised extract was run through, the column was washed with 10 ml of water and the phosphorylated intermediates were eluted with 0.05 N formic acid, collecting in an automatic fraction collector at a rate of 5 ml in 10 min. per tube. When only phosphocreatine was required, the column was washed with 25 ml of 0.05 N followed by 25 ml of 1.5 N formic acid before elution of the phosphocreatine with 0.5 N formic acid.

H. F. W. KIRKPATRICK

2818. The distribution of lipid and phospholipid in paper electrophoresis of normal serum lipoproteins. M. A. Chapin (Central Maine Gen. Hosp., Lewiston, Me., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (3), 386-391.—A detailed procedure is given for carrying out the paper electrophoresis and methods of staining the resulting paper strips are described. A study is made of the distribution of alpha- and beta-lipids and of the proportions of phospholipids in the total lipids of normal blood samples.

W. H. C. SHAW

2819. Qualitative researches on ribonucleic acids of tissue. I. Method of estimation of ribonucleotides without previous purification of the ribonucleic acid. P. Mandel, J. D. Weill and M. Ledig (Inst. Chim. Biol., Strasbourg). *Bull. Soc. Chim. Biol.*, 1956, **38** (1), 71-80.—Organs frozen and weighed soon after removal are extracted with 7 per cent. trichloroacetic acid in the cold, and a sample of the residue containing 700 to 1000 μg of ribonucleic phosphorus is hydrolysed for 15 hr. at 37° C with N/3 NaOH. After acidification with 65 per cent. HClO_4 and separation of the ppt., 10-ml portions of the solution are carefully neutralised, 1.5 ml of 20 per cent. Pb acetate are added, and the ppt. is allowed to form overnight. A suspension of the

washed ppt. in water is treated with H_2S and the PbS is separated. The H_2S in the filtrate is removed by heating on the water bath, and the solution is made up to 50 ml. Part of the solution is set aside for a control estimation of P and the remainder is evaporated to dryness under reduced pressure at $65^\circ C$ then taken up with 0.1 N HCl. The solution is chromatographed for 48 hr. on paper with *n*-propanol - aq. NH_3 - water (6:3:1). The paper is dried and examined under u.v. light, when spots of guanylic, uranylic, cytidylic and adenylic acids appear in that order. The starting line is cut off, as phosphate ions remain there and would move with the next solvent, and the chromatogram is run again in the same direction for 15 to 18 hr. with isobutyric acid - 0.5 N aq. NH_3 (5:3). Another spot appears further down the strip, which is not a ribonucleotide. The spots are cut up and extracted with 0.1 N HCl for 15 hr. at $37^\circ C$ and the extinction is measured against a 0.1 N HCl blank at 280 $m\mu$ for cytidylic acid and 260 $m\mu$ for the others. A phosphorus determination is also carried out. The accuracy of this and other methods is discussed. E. J. H. BIRCH

2820. Nephelometric determination of adenine and guanine. W. Leyko and B. Filipowicz (Akad. Med., Łódź, Poland). *Roczn. Chem.*, 1955, **29** (4), 1095-1101.—The adenine content of a pancreas hydrolysate is determined polarographically, and an aliquot containing 24 μg of adenine is used for the nephelometric determination of total adenine and guanine according to the method of Groves and Kober (*J. Amer. Chem. Soc.*, 1915, **37**, 3430). The guanine content of the aliquot is read from an empirical curve relating turbidity with guanine content of a series of solutions containing 24 μg of adenine and 24 to 83 μg of guanine. R. TRUSCOE

2821. Colour reaction of amino acids with alloxan, isatin and ninhydrin in circular-paper chromatography. A. Saifer and I. Oreskes (Isaac Albert Research Inst., Jewish Chronic Disease Hospital, Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 501-504.—The colour reactions and sensitivities as spot-reagents on filter-paper are given for alloxan (I), isatin (II) and ninhydrin (III) with 51 amino acids. R_f values for these amino acids were determined by circular-paper chromatography, with phenol - water (0.1 per cent. of aq. NH_3) and butanol - acetic acid - water (40:10:50) as developing solvents. II gives a wide variety of colours with different amino acids, and no colour at all with many, and is useful for differential determinations. I gives more stable colours and in some cases is more sensitive than III. The nature of these colour reactions is discussed. A. R. ROGERS

2822. The estimation of arginine. H. Rosenberg, A. H. Ennor and J. F. Morrison (John Curtin Sch. of Med. Res., Austral. Nat. Univ., Canberra, Australia). *Biochem. J.*, 1956, **63** (1), 153-159.—A colorimetric method is described for the determination of 10 to 100 μg of arginine. It is a modification of that of Eggleston *et al.* (*Brit. Abstr. C*, 1944, 29). Development of the colour in the presence of *n*-propanol and an increased concn. of 1-naphthol increases the sensitivity of the method for mono-substituted guanidines to that previously obtained with di-substituted guanidines. The method, which is applicable to other guanidino compounds, including streptomycin, is suitable for the determination of arginine in proteins. J. N. ASHLEY

2823. The determination of tryptophan in natural media. I. Stability of tryptophan to hydrolysing agents. A. Drèze (Lab. de Biochim., Univ. Libre de Bruxelles). *Bull. Soc. Chim. Biol.*, 1956, **38** (1), 243-253.—Tryptophan is heated for 20 hr. at $120^\circ C$ in 5 N NaOH or 6 N Ba(OH) $_2$ in sealed tubes under N, alone or in the presence of $SnCl_2$, EDTA (disodium salt) or cysteine hydrochloride as stabilising agent. The heating is repeated at $100^\circ C$, both under N and in air. At $120^\circ C$, only the experiment in the presence of $SnCl_2$ permits a quant. recovery of tryptophan; at $100^\circ C$ the tryptophan is much more stable. The tryptophan is purified, after the treatment, by chromatography on potato starch and is determined colorimetrically. The methods of hydrolysis used by various authors are critically discussed. E. J. H. BIRCH

2824. Detection and determination of cysteine in wool with 1-fluoro-2:4-dinitrobenzene. H. Zuber, K. Traumann and H. Zahn (Chem. Inst. Univ. Heidelberg). *Z. Naturforsch.*, 1955, **10b** (8), 457-462.—At values below pH 5.5, fluorodinitrobenzene reacts at room temperature with only the mercapto group of cysteine and not with the amino group. The S-(2:4-dinitrophenyl)cysteine (I) is not decomposed by the action of 6 N HCl at $105^\circ C$ during 24 hours' heating, nor is it affected by chromatographic mixtures containing butanol, formic acid or phenol. The dinitrophenyl protein derivative is formed by heating 1 g of wool with 1 g of fluorodinitrobenzene in 100 ml of acetate buffer of pH 5.2 at $60^\circ C$ for 3 hr., replacing the solution with fresh solution after this time and heating for another 3 hr. The wool is then washed exhaustively, finally with 0.1 N HCl for 10 to 20 hr. to remove adsorbed dinitrophenols, then dried and extracted with acetone in a Soxhlet apparatus. The treated wool (200 mg) is then dried at $105^\circ C$ for 2 hr. and weighed after being set aside for 1 hr. The product is then submitted to hydrolysis in a sealed tube with 2 ml of 6 N HCl at $105^\circ C$ for 15 to 20 hr. The hydrolysate is filtered and washed well and combined filtrate and washings are reduced to a small volume in a vacuum and freed from the last traces of HCl by aeration for 30 min. The hydrolysate (0.1 ml) is applied to a strip of filter-paper (80 cm \times 14 cm) and electrophoresis is carried out in a buffer of formic and acetic acids (pH 1.93) at 6000 V (6 to 8 mA) for 180 min. at $-5^\circ C$. The strip is then dried and scanned in u.v. light to mark the I. The area is cut out from the paper and the I is eluted with 0.03 N HCl, warming slightly. The extinction value of this solution is read between 320 and 340 $m\mu$ in a spectrophotometer. The values obtained with this method, after applying correction factors, do not agree with those obtained with colorimetric procedures. For untreated wool the cysteine content is found to be only a third of that obtained by the colorimetric method, whereas that of wool treated with KCN is three times as high. E. KAWERAU

2825. Spectrophotometric analysis of proteins by a selective filter technique. E. Annau (Animal Diseases Research Inst., Hull, Quebec, Canada). *Canad. J. Biochem. & Physiol.*, 1956, **34** (2), 236-241.—Xanthine solutions at pH 11 have an absorption in the region 260 to 300 $m\mu$ similar to that of proteins at pH 7.3 and 10, so that its use as an optical filter enables the fine structure of the protein spectrum to be revealed. Absorption spectra are mapped for bovine-serum albumin, egg albumin, casein and gelatin at pH 7.3 and 10, with 2 to 6

$\times 10^{-5} M$ xanthine in 0.001 M NaOH as filter. The fine-structure maxima and minima are observed and compared with those obtained by other workers with more complex methods, and good agreement is obtained. The method can be used for the spectrophotometric identification of proteins.

E. J. H. BIRCH

2826. A comparison of two commonly used "salt-fractionation" methods for differential plasma protein estimation. J. K. Fawcett and V. Wynn (St. Mary's Hosp., London). *J. Clin. Pathol.*, 1956, **9** (1), 71-74.—In the determination of albumin and globulin in plasma the results obtained by salting-out the globulin with Na_2SO_4 at concn. of 22 and 26 per cent. have been compared. Little difference was found in respect of reproducibility of results, and the separation of the results into diagnostic patterns was only slightly better with 26 than with 22 per cent. Na_2SO_4 . This slight advantage, however, coupled with the observation of other workers that the results with 26 per cent. Na_2SO_4 are closer to those given by electrophoresis, appears to be a good reason for giving it preference.

H. F. W. KIRKPATRICK

2827. Determination of protein-bound radioiodine with an anion-exchange resin. L. Zieve, W. C. Vogel and A. L. Schultz (Veterans Admin. Hosp., Minneapolis, Minn., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (4), 663-668.—Loss of protein-bound ^{131}I in a standard procedure requiring pptn. of proteins and the washing of the ppt. with trichloroacetic acid was found to be about 15 per cent. In the method proposed, inorganic I is removed by a single passage through a column of Amberlite IRA-400 (OH) resin converted to the chloride form by the procedure described. Results by the proposed method differ by about 4 per cent. from those obtained by dialysis.

W. H. C. SHAW

2828. The sublimate test as a micro-method for the determination of γ -globulin in serum. M. Keler-Bačoka (Univ. Clinic, Zagreb, Yugoslavia). *Mikrochim. Acta*, 1956, (1-3), 237-243.—Details are given of the Keler-Bačoka and Dević-Mikač sublimate test which is specific only for raised γ -globulin values. *Soln. required*—(i) 9.078 g of KH_2PO_4 in H_2O to 1 litre. (ii) 11.876 g of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ in H_2O to 1 litre. (iii) Mix 28 ml of soln. (i) with 72 ml of soln. (ii). (iv) Sublimate soln.—0.047 per cent. HgCl_2 in H_2O . *Procedure*—To 5 ml of soln. (iii) add, by micro-pipette, 0.10 ml of serum. Add 0.4 ml of soln. (iv) and mix. Run a blank to compensate for the serum colour by mixing 5.4 ml of soln. (iii) and 0.1 ml of serum. Measure the extinction at 430 $m\mu$ after 20 min. in a Pulfrich photometer in a 10-mm cell. $E/0.07 =$ sublimate units (normal values 1 to 5). Plot the calibration curve with BaSO_4 by the Shank and Hoagland thymol procedure. An investigation made of the sublimate test ppt. by paper electrophoresis showed (a) the positive test is specific only for raised γ -globulin values; (b) other globulin fractions, i.e., α_1 , α_2 and β fractions, are not carried down by the test, even in strongly increased concentrations; (c) possibilities exist for obtaining and isolating larger quantities of γ -globulin from the serum by means of the sublimate test.

D. F. PHILLIPS

2829. A micro-assay for plasma fibrinogen. H. D. Wycoff (Univ. Wisconsin, Madison, U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (4), 645-648.—In a modified procedure for use with 0.1 ml of plasma, the fibrino-

gen is pptd. by treatment with a commercial thrombin preparation dissolved in 0.85 per cent. aq. NaCl containing 10 per cent. v/v of ethanol. The fibrin is collected on a tared glass needle, washed, dried and weighed. Alternatively the fibrin may be digested with H_2SO_4 and aq. H_2O_2 and the resulting $(\text{NH}_4)_2\text{SO}_4$ determined colorimetrically with Nessler reagent.

W. H. C. SHAW

2830. Fluorimetric estimation of oestrogens in bovine urine. E. P. Smith, W. M. Dickson and R. E. Erb (Washington State Coll., Pullman, U.S.A.). *J. Dairy Sci.*, 1956, **39** (2), 162-170.—A method for the extraction, purification and fluorimetric detn. of phenolic oestrogens in the urine of cattle is given. When applied to the urine of pregnant cows, increasing amounts of fluorescent substances were found as pregnancy advanced, but biological assays indicated that only about a quarter of the observed fluorescence was due to biologically active oestrogens.

W. H. C. SHAW

2831. Observations on the occurrence of 16-epioestriol in urine. [Determination.] E. J. D. Watson and G. F. Marrian (Dept. of Biochem., Univ. of Edinburgh). *Biochem. J.*, 1956, **63** (1), 64-69.—A modified Kober chromogen method is described for the determination of 16-epioestriol in the urine from normal menstruating women and pregnant women.

J. N. ASHLEY

2832. Refinements in the determination of "free pregnanediol." E. L. Saier, R. C. Graver and H. S. Strickler (Allegheny Gen. Hosp., Pittsburgh, Pa., U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1956, **16** (4), 535-541.—Urine specimens were boiled for 15 min. with 10 per cent. by vol. of conc. HCl and extracted with benzene or ether. The neutral fraction was further fractionated with Girard's reagent T and the non-ketonic neutral fraction was dissolved in toluene. Purification and pptn. of the pregnanediol was then carried out by the procedure of Talbot *et al.* (*J. Clin. Endocrin.*, 1941, **1**, 668). The use of Girard's reagent gave a purer product containing no digitonin-precipitable material, and the determinations by colorimetric and fluorimetric methods were in good agreement. The H_2SO_4 colour reaction with the final residue is more specific for pregnanediol than is the gravimetric procedure. Extraction with ether yielded higher results than that with benzene.

H. F. W. KIRKPATRICK

2833. Estimation of urinary reducing corticosteroids with blue tetrazolium. H. Sulkowitch, A. M. Rutenburg, M. F. Lesses, S. Cargill and A. M. Seligman (Beth Israel Hosp., Boston, Mass., U.S.A.). *New Engl. J. Med.*, 1955, **252**, 1070-1075.—A simple method is described for estimating total corticosteroids (I) in 50 ml of urine after enzymic hydrolysis with β -D-glucuronidase. It depends on reduction of blue tetrazolium (II) and is rendered more sensitive than previous methods by the use of an increased concn. of hot alkali and, as solvent, diethylene glycol dimethyl ether, purified by vacuum-distillation from LiAlH_4 . The reactions with II were positive with cortisone and dehydrocorticosterone but only half as strong with hydrocortisone, corticosterone and deoxycorticosterone. Steroids that failed to react included those conjugated with H_2SO_4 , as well as 3:20-allopregnandione, dehydroisoandrosterone, cholesterol, one of the norcholestenols, 3:7-androstanedione, cholestanone, oestrone, Δ^3 -3:20-pregnenolone, pregnandione, 3-hydroxy-11-oxo-aetiocholic acid methyl

ester and oestradiol. The urinary excretion of **I** per 24 hr. for normal males and females was 4.1 to 7.5 mg.

CHEM. ABSTR.

2834. Comparison of a radioactive-isotope technique with techniques using flame photometry in the bio-assay of mineralocorticoids. J. G. Llauro (Otago Med. Sch., Dunedin, New Zealand). *Endocrinology*, 1956, **58** (3), 390-392.—Results obtained in the biological assay of deoxycorticosterone acetate with ^{22}Na and ^{42}K are compared with those in which ordinary Na and K are determined by two methods requiring flame photometry. It is concluded that all the three methods are equally reliable and that the use of radioactive isotopes for the assay of electrolyte-regulating corticosteroids has no advantage.

W. H. C. SHAW

2835. The chromatographic separation of the glucuronides of urinary steroid ketones. R. W. H. Edwards and A. E. Kellie (Courtauld Inst. Biochem., Middlesex Hospital Med. Sch., London). *Chem. & Ind.*, 1956, (14), 250-251.—Separation of urinary androsterone and aetiocholanolone as glucuronides has been accomplished by preparing a dry extract, subjecting it to a Girard separation, and chromatographing the purified ketonic conjugates on silicic acid. The silicic acid column contained 0.6 ml per g of aq. sodium acetate (0.1 N) as stationary phase and elution was effected with chloroform containing 2 per cent. v/v of ethanol and 0.4 per cent. v/v of acetic acid. The elution rate was 2 ml per hr., fractions of 2 ml being collected automatically and portions tested for 17-ketosteroid (Zimmermann reaction) and glucuronic acid (1:3-dihydroxynaphthalene reaction).

H. F. W. KIRKPATRICK

2836. Deuterisation of steroids and their use in isotope-dilution analysis. S. L. Jones, I. D. Robinson, B. H. Arison and N. R. Trenner (Res. Lab., Merck & Co. Inc., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part I), 482-483.—An isotope-dilution assay for the determination of 17-hydroxy-11-deoxycorticosterone (**I**) and 17-hydroxycorticosterone (**II**) in liquors from microbial oxidations is described. Deuterium was used as the tracing isotope and was introduced by a technique similar to that of Fukushima and Gallagher (*J. Biol. Chem.*, 1952, **198**, 871), a platinum catalyst and 70 per cent. deuterio-acetic acid being used. On a known broth containing 68.2 mg of **I** and 87.5 mg of **II**, 64 mg and 90 mg, respectively, were recovered. Known amounts of deuterio-**I** and deuterio-**II** were added to the fermentation liquor, mixed, extracted, separated, and purified, and the original content of the broth was then calculated from the dilution of the deuterium in the isolated steroids. Data on the catalytic introduction of deuterium into several new steroids, some of them cortical hormones, are given.

K. A. PROCTOR

2837. The enzymic synthesis of steroid sulphates. [Assay of the soluble enzyme.] A. B. Roy (Dept. of Biochem., Univ. of Edinburgh). *Biochem. J.*, 1956, **63** (2), 294-300.—A method is described for the assay of steroid sulphate synthesised by a soluble enzyme preparation from rat liver. Dehydroepiandrosterone is used as substrate, but any suitable steroid is an alternative substrate. The method is a micro-modification of that of Roy (*Biochem. J.*, 1956, **62**, 41), which makes use of the solubility in CHCl_3 of the complexes formed between methylene blue and ethereal sulphates.

J. N. ASHLEY

2838. The nature of the initial reaction of oxygen with two bacterial cytochrome oxidases. [Determination of oxygen.] I. S. Longmuir and B. J. Clarke [Microbiol. Res. Dept. (Ministry of Supply), Porton, Wilts., England]. *Biochem. J.*, 1956, **63** (1), 57-61.—A polarographic method is described for the determination of oxygen in acid soln. by means of a rotating gold electrode.

J. N. ASHLEY

2839. Studies on succinic dehydrogenase. I. Preparation and assay of the soluble dehydrogenase. E. B. Kearney and T. P. Singer (with N. Zastrow) (Univ. of Wisconsin, Madison, Wis., U.S.A.). *J. Biol. Chem.*, 1956, **219** (2), 963-975.—A simple manometric method is described for the determination of soluble dehydrogenase activity in preparations from various animal tissues. Cytochrome *c* and the dyes normally used for the assay of mitochondrial preparations of the dehydrogenase do not react with the soluble enzyme and ferricyanide is a relatively poor acceptor. The method depends on the use of phenazine methosulphate, and involves manometric determination of the oxygen uptake by the system in the presence of 10^{-3}M CN^- , $2 \times 10^{-2}\text{M}$ succinate, $5 \times 10^{-2}\text{M}$ phosphate (pH 7.6), and phenazine methosulphate (2 mg) in a final vol. of 3 ml at 38°C. The substrate and the dye are placed in the side arm of a Warburg vessel and must be tipped simultaneously because in the absence of succinate the dye readily inactivates the enzyme.

J. N. ASHLEY

2840. The fluorimetric determination of β -glucosidase: its occurrence in the tissues of animals, including insects. D. Robinson (St. Mary's Hosp. Med. Sch., London). *Biochem. J.*, 1956, **63** (1), 39-44.—4-Methylumbelliferone β -D-glucoside is used as a substrate in a fluorimetric method for the determination of β -glucosidase. The method is rapid, simple, and very sensitive. The intensity of the fluorescence of the liberated 4-methylumbelliferone is measured against a quinine standard by means of a Spekker absorptiometer with fluorimetry attachment.

J. N. ASHLEY

2841. Determination of glyoxalase activity. G. R. McKinney and D. J. Gocke (West Virginia Univ. Sch. of Med., Morgantown, W. Va., U.S.A.). *J. Biol. Chem.*, 1956, **219** (2), 605-610.—A simple colorimetric method is described for the determination of glyoxalase activity in extracts of rat liver and suspensions of leucocytes from dog blood. The method is a micro-modification of that of Ariyama (*Brit. Abstr. A*, 1928, 796), manometry being replaced by colorimetry. Methylglyoxal is used as a substrate, and the method depends on its ability to reduce Benedict's uric acid reagent (tungstoselenophosphoric acid), the colour being measured spectrophotometrically at 705 m μ . The method will determine 2 μg of methylglyoxal. Glyoxal and phenylglyoxal reduce the reagent, and uric acid and ascorbic acid give a colour in the system.

J. N. ASHLEY

2842. Carbohydrate metabolism in citric acid fermentation. IV. Purification and properties of aldolase from *Aspergillus niger*. [Determination of aldolase.] V. Jagannathan, K. Singh and M. Damodaran (Nat. Chem. Lab. of India, Poona, India). *Biochem. J.*, 1956, **63** (1), 94-105.—A new spectrophotometric method for the determination of aldolase activity is described. When aldolase and fructose 1:6-diphosphate are mixed in the presence of small amounts of hydrazine, the rate

of increase in the extinction at 240 μ is proportional to enzyme concn. Hydrazine can be replaced by semicarbazide, but not by hydroxylamine. The method is similar in sensitivity to that of Warburg and Christian but it has the advantage that it can be used in the presence of enzymes which oxidise or destroy reduced diphosphopyridine nucleotide and interfere with the other method. The test system is also less complex and contains only the enzyme, substrate and hydrazine.

J. N. ASHLEY

2843. Viscosimetric method for comparing the activities of hyaluronidase and a standard. W. Daubenmerkl (Copenhagen Univ., Denmark). *Acta Pharm. Tox., Kbh.*, 1956, **12** (1), 65-80.—The method described is based on a comparison of the reduction in viscosity of a substrate containing hyaluronic acid at pH 6.8 when incubated with unknown and standard hyaluronidase preparations. Viscosities are measured from the flow times on 1-ml amounts in a U-tube viscometer at 37° C on the substrate without enzyme and then at suitable intervals after the addition of enzyme, so that the flow time after incubation for 350 sec. can be calculated. Determinations are carried out at three different enzyme concentrations, which are approx. the same both for the standard and unknown samples. A rectilinear relationship is obtained between the reduction in viscosity calc. by the methods given and the log. of the enzyme concentration for both unknown and standard preparations; from the ratio of their activities that of the unknown is calculated. The necessary apparatus and reagents are described and an assessment is made of the accuracy of the method. Details are given for the preparation of the substrate from crude hyaluronic acid obtained from bovine synovial fluid or from purified potassium hyaluronate.

W. H. C. SHAW

See also Abstracts 2656, 2725, 2771, 2772, 2773, 2850, 2863, 2930, 2931, 2933.

Drugs

2844. The use of micro-methods in the analysis of special pharmaceutical products. S. Simon (Serv. Contrôle des Médicaments, Ass. Pharm. Belge, Brussels). *Mikrochim. Acta*, 1956, (1-3), 118-124.—A review is given of the large range of applications for microchemical methods in the control of medications. The speed and high relative accuracy of such techniques make their use almost indispensable, and have resulted in a progressive supplantation of the more classical methods.

D. F. PHILLIPS

2845. Titration of drugs and chemicals in non-aqueous solution. VI. Determination of morphine, its derivatives and their acid salts in glacial acetic acid. Tetsu Kashima, Haruyo Asahina and Yoshihiko Shiuchi (Nat. Hyg. Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (3), 329-332.—Morphine (I) and its derivatives are more basic towards HClO_4 in glacial acetic acid (II) than in an aq. soln., owing to the methylamine group. I (>0.1 g) is titrated as a monoacidic base in II with HClO_4 with crystal violet as an indicator (error <0.1 per cent.). The chloride (less sol. in II) is also titrated in the presence of an amount of Hg^{II} acetate greater than the equiv. of I. No interference results from the presence of sugars, starch, talc and alcohols.

Inorganic radicles other than Cl^- increase the error 10 times.

VII. Determination of antihistamine drugs (derivatives of dimethylaminoethane) and their basicity in glacial acetic acid. Tetsu Kashima. *Ibid.*, 1955, **75** (3), 332-335.—The titration of antihistamine drugs, including diphenhydramine hydrochloride (III), doxylamine succinate, chlorphenylpyridamine maleate, tripeleminamine hydrochloride and Antergan hydrochloride (IV), was studied by the use of HClO_4 (0.02 to 0.05 N) in II, in the presence of mercuric acetate. The mercuric acetate does not vitiate the titration except with IV. Both III and IV behave as monoacidic bases whilst others as diacidic. Since maleic acid does not show an acidic nature in II, the addition of mercuric acetate for salts of this acid is not necessary. The error for most of them is <0.1 per cent., but for IV is <0.5 per cent. Crystal violet (0.5 per cent. in II) is the best indicator.

K. SAITO

2846. Polarimetric and paper-chromatographic detection of laevo- and dextro-rotatory alkaloids in ergot. F. Gstirner and H. O. Müller (Pharm. Inst. Univ. Bonn, Germany). *Arch. Pharm., Berlin*, 1955, **288**, 589-595.—The alkaloids are isolated from 100 g of the powdered drug after de-fatting with light petroleum, by extraction with ammoniacal ether soln. (120 ml of ether and 2 ml of a 10 per cent. aq. NH_3 soln.) in a Soxhlet apparatus. The ether soln. (50 to 100 ml) is shaken with a 1 per cent. tartaric acid soln. (3×15 ml), the aq. soln. being subsequently treated with 2 to 3 g of NaHCO_3 , when the water-sol. compounds are separated from the insol. compounds, which are then shaken with ether (3×20 ml), the solvent being then allowed to evaporate and the residue dried *in vacuo*. The purified alkaloid is dissolved in chloroform and the optical rotation is determined. A simple circular paper-chromatographic procedure is also described, in which a chloroform soln. of ergotamine, ergocristine, ergotamine and ergocristine, containing 50 μ g of alkaloid, is separated on paper treated with a citric acid-phosphate buffer soln. of pH 5.6. The developing liquid is benzene-90 per cent. ethanol (9:1), the separation taking about 4 hr. The following R_F values are given—ergotamine, 0.37; ergocristine, 0.49; ergotamine, 0.59; and ergocristine, 0.69.

G. R. WHALLEY

2847. The chemical evaluation of *Rauwolfia serpentina* preparations. J. Carol, D. Banes, J. Wolff and H. O. Fallscheer (Div. Pharm. Chem., Food and Drug Admin., Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (4), 200-203.—Methods are presented for the identification and assay of *Rauwolfia serpentina* root and its preparations. The assay is based on partition chromatography on Celite 545, with aqueous ethanolic citrate buffer as stationary phase, and the upper layer of an isooctane- CHCl_3 - H_2O -ethanol (10:5:5:2) mixture as mobile phase; a fraction of the eluate containing reserpine and rescinnamine is saponified, and the liberated trimethoxybenzoic and trimethoxysalicylic acids are extracted into CHCl_3 and determined spectrophotometrically (270 and 300 μ). *R. serpentina* can be distinguished from other species by paper chromatography of an ethanolic extract, with either a heptane- CCl_4 -formamide-*tert*-butyl alcohol mixture in the presence of NH_3 vapour, or a benzene-*isooctane*-formamide mixture, as mobile phase, and a 30 per cent. soln. of formamide in acetone as stationary phase. The chromatograms are examined in u.v.

light after being sprayed with a soln. of trichloroacetic acid (5 g) and sodium nitroprusside (25 mg) in methanol (100 ml) (*cf.* Banes *et al.*, *Anal. Abstr.*, 1956, 3, 1480).

A. R. ROGERS

2848. Micro-determination of lupanine and hydroxylupanine. I. Reifer and M. Mozejko (Biochem. Lab., I.U.N.G., Warsaw, Poland). *Roczn. Chem.*, 1955, 29 (4), 1087-1094.—A modified Mayer reagent, prepared by dissolving CdI_2 (2.4 g), HgI_2 (6.5 g) and NaCl (20 g) in 100 ml of boiling water, boiling, and filtering, is used for pptg. lupanine and hydroxylupanine, separately or together. Both alkaloids are pptd. by this reagent in strongly acid soln., but at pH 4.5 only lupanine is pptd. The separate determination is based on this. The alkaloids are determined by treating with Br, removing the excess and then reacting with KI. The I liberated is titrated. R. TRUSCOE

2849. A simplified assay of nux vomica tincture. M. Scott, A. Taub and C. Piantadosi (Coll. Pharmacy, Columbia Univ., N.Y., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, 45 (4), 232-236.—A procedure is described for the assay of tincture of nux vomica for strychnine (I) and brucine (II), which involves purification by adsorption on alumina, cation exchange and spectrophotometry. The results compare favourably with those by the (U.S.) N.F. method and are obtained more rapidly. *Procedure*—Stir the sample (5 ml) with 70 per cent. ethanol (5 ml) and alumina (10 g) for 5 min. Filter and dilute the filtrate to 50 ml with 70 per cent. ethanol. Adjust a 10-ml aliquot to pH 9 or 10 with aq. NH_3 , and add it to Amberlite IRC-50 (H) resin (10 ml), which has been prepared by steam-distillation and repeated washes with alkali and acid. Stir the mixture for 15 min., and decant through a filter-paper, washing with 70 per cent. ethanol (2 x 10 ml); reject the filtrate and washings. Extract the resin with 0.1 N HCl in 70 per cent. ethanol (4 x 25 ml) at 80° C and pass the extracts through the same filter-paper. Dilute a 10-ml aliquot to 50 ml with H_2O , mix, and filter through a Selas No. 010 crucible. Measure the extinctions at 255 and 264 $m\mu$ against a similarly treated blank. $E_{255} = 346.9 c_I + 215.0 c_{II}$, and $E_{264} = 289.9 c_I + 299.9 c_{II}$, where c_I and c_{II} are concn. of I and II, respectively.

A. R. ROGERS

2850. Determination of catalase in tobacco. A. Ollero Gómez and A. Paneque Guerrero (Inst. Tobacco Biol., Seville, Spain). *An. Real Soc. Esp. Fis. Quim.*, 1956, 52B (1), 51-62.—The application of several methods of catalase determination in tobacco is studied. The titration method of the residual substrate, with permanganate, has given rise to considerable errors. The Balls and Hale method (*J. Ass. Off. Agric. Chem.*, 1932, 15, 483) gives good results except with tobaccos of low activity. A gasometric method, making use of the Warburg technique, is described. This method is considered to be the best available. The technique is described in detail, with several curves showing the relation between concn. and oxygen evolved in the determination.

C. A. FINCH

2851. A paper-chromatographic and fluorimetric method for determining the cardiac glycosides and aglycones of *Digitalis purpurea*. K. B. Jensen (Pharm. Inst., Oslo Univ., Norway). *Acta Pharm. Tox., Kbh.*, 1956, 12 (1), 27-46.—The previously described paper-chromatographic separation (*Anal. Abstr.*, 1954, 1, 1629; 1956, 3, 2852) and the fluori-

metric method (*Anal. Abstr.*, 1954, 1, 1628) for the determination of pure digitalis glycosides are combined, modified and extended for the analysis of digitalis leaves. *Purpurea* glycosides A and B, digitoxin, gitoxin, digitalinum verum, gitorin, strospeside, digitoxigenin and gitoxigenin are determined, and the scheme also includes various unknown substances that can be converted into known glycosides by hydrolysis with digipurpidase or by treatment with NaHCO_3 in aq. methanol (*Anal. Abstr.*, 1956, 3, 2853). Details are given for the preparation of tinctures of the powdered leaf samples by percolation with 70 per cent. ethanol. Apart from a small change from unknown to known glycosides, the tinctures are shown to be stable for at least one year. Purified glycoside concentrates for chromatographic analysis are prepared from the tinctures by extraction with light petroleum, or, more efficiently, but with more conversion of unknown to known glycosides, by treatment with lead subacetate. The effect of the solvent used for preparing the concentrates is studied and those made with isopropyl alcohol are shown to be stable. The sensitivity, specificity, accuracy and precision of the methods described are investigated and discussed. The determination of an A- or a B-series glycoside is shown to be unaffected by the presence of glycosides of the other series, and digitonin does not interfere. With digitoxin (A series) and gitoxin (B series) reproducibility is shown to be good, and when tested with seven known substances no detectable loss was observed during the determinations.

W. H. C. SHAW

2852. Paper-chromatographic detection of new components in the glycoside complex of *Digitalis purpurea*. K. B. Jensen (Pharm. Inst., Oslo Univ., Norway). *Acta Pharm. Tox., Kbh.*, 1956, 12 (1), 11-19.—The procedure with formamide-impregnated filter-paper described previously (*Anal. Abstr.*, 1954, 1, 1629) is modified for the detection of digitalinum verum, gitoxin and strospeside. These three glycosides are separated by development with chloroform-acetone (8:2) to which just sufficient formamide is added to ensure saturation. Several unknown substances were also detected in leaf extracts with this solvent. The classification of unknown glycosides according to their ability to hydrolyse with digipurpidase (*Anal. Abstr.*, 1954, 1, 1630) is shown to be inadequate, and a modified classification based on hydrolysis to digitoxigenin (A series) or gitoxigenin (B series) is proposed.

W. H. C. SHAW

2853. Isolation by paper chromatography of unknown glycosides from *Digitalis purpurea* and their transformation into the known cardiac glycosides. K. B. Jensen (Pharm. Inst., Oslo Univ., Norway). *Acta Pharm. Tox., Kbh.*, 1956, 12 (1), 20-26.—Details are given of the hydrolysis of unknown substances of the A series of digitalis glycosides (*Anal. Abstr.*, 1956, 3, 2852) with digipurpidase to give digitoxin, and of the B series with NaHCO_3 in aq. methanol to give digitalinum verum, purpureaglycoside B, strospeside and gitoxin.

W. H. C. SHAW

2854. Determination of some derivatives of hydroxyanthraquinones by titration in non-aqueous solvents. A. Anastasi, U. Gallo and E. Mecarelli (Farmitalia, Milan). *Mikrochim. Acta*, 1956, (1-3), 252-256.—A method of potentiometric titration with sodium methoxide is described for the determination of derivatives having constitutions similar to

that of 1:8-dihydroxyanthraquinone, 1:8-dihydroxy-3-methylanthraquinone and 1:8-dihydroxy-3-methylanthrone. Pyridine is used as solvent. As the intense self-colour of the solutions prevents the use of indicators, the end-point is determined by use of a glass-antimony electrode pair. The results reported show good reproducibility.

D. F. PHILLIPS

2855. Methods of distinguishing cassia and Japanese cinnamons. Jobu Higashi, Kan-ichi Mizobuchi and Setsuko Fujii (Faculty of Pharm., Tokushima Univ., Sho-machi, Tokushima). *J. Pharm. Soc. Japan*, 1955, **75** (3), 347-350.—Differentiation of powders of cassia bark (*Cinnamomum cassia*) (I) and *C. loureirii* (II) was studied by capillary analysis. The sample is extracted and submitted to paper chromatography in 60 per cent. ethanol, the spots being tested with N NaOH or 0.1 per cent. pyronine (III) under daylight or u.v. light. When a particular zone is spotted with III, I shows an orange fluorescence, whilst II gives a red colour.

K. SAITO

2856. Differentiation of tetracycline, oxytetracycline and chlortetracycline. O. N. Yalcindag (Istanbul Univ.). *Amer. J. Pharm.*, 1955, **127** (10), 362-364.—Capillograms of tetracycline hydrochloride with AgNO_3 and FeCl_3 are different from those of chlortetracycline and oxytetracycline and afford a method for the differentiation of the three antibiotics, which can also be differentiated by reagents such as FeCl_3 , formaldehyde and conc. H_2SO_4 , and conc. H_2SO_4 .

I. JONES

2857. Analysis of phenobarbitone in pharmaceuticals by argentimetric potentiometric titration. J. I. Bodin (Univ. of Wisconsin, Madison, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (3), 185-187.—The potentiometric determination of phenobarbitone is based on the quant. reaction of molar Ag^+ with molar barbiturate to form a slightly dissociated salt which is sol. in Na_2CO_3 soln. At the end-point, the excess of Ag^+ precipitates as Ag_2CO_3 ; thus the end-point potential is that of a satd. soln. of Ag_2CO_3 in the presence of an excess of CO_3^{2-} . The end-point potential of a freshly prepared standard is determined at the time of each titration. *Procedure*—Prepare a standard blank soln. from ethanol (95 per cent.) (10 ml), Na_2CO_3 soln. (3 per cent.) (50 ml), 0.01 N AgNO_3 soln. (1 ml) and water to 100 ml. Determine its potential, which should be 232 ± 12 mV vs. the S.C.E. In the assay of Elixir Phenobarbital U.S.P. reduce the ethanol content of the blank to 7 ml. *For phenobarbitone soln.*—Mix a sample (≈ 200 mg of phenobarbitone) with ethanol (95 per cent.) (10 ml), add Na_2CO_3 soln. (3 per cent.) (50 ml) and adjust to 100 ml with water. Titrate with 0.1 N AgNO_3 to the standard blank potential. *For Elixir Phenobarbital U.S.P.*—Mix 50 ml of sample with 50 ml of Na_2CO_3 soln. (3 per cent.). Determine the potential of the special standard and titrate to this potential. *For tablets and capsules*—Transfer a weighed sample (≈ 500 mg of phenobarbitone) to a 250-ml calibrated flask by means of ethanol (25 ml); add water (25 ml), swirl to disperse the insol. matter, add Na_2CO_3 soln. (3 per cent.) (125 ml), shake well and adjust to volume. Filter, rejecting the first 25 ml, and collect 100 ml. Titrate to standard potential. To correct for the blank, subtract 0.1 ml from the vol. of 0.1 N AgNO_3 used for the titration. The method is not applicable in the presence of halides and NH_4^+ , or Na, Ca and Mg

steates. The procedure is rapid and accurate to within ± 0.3 per cent.

H. B. HEATH

2858. Chromatography and detection of certain substituted hydantoins. J. P. Vigne and J. Fondarai (Lab. des Isotopes de Lutte contre le Cancer de Marseille). *Bull. Soc. Chim. France*, 1956, (1), 124-125.— R_F values are quoted for 5-ethyl-5-phenyl-, 5-ethyl-3-methyl-5-phenyl-, 5:5-diphenyl- and 3-methyl-5:5-diphenyl-hydantoin chromatographed on paper with butanol (saturated with N HCl), butanol (saturated with 4 N aq. NH_3), pentane-pyridine (100:1) (saturated with benzyl alcohol and water) or hexane-pyridine (100:1) (saturated with benzyl alcohol and water), with the ascending technique. The spots are applied to the strip, which is then finely sprayed with water from a distance and left in the enclosed chamber for 1 hr. before being dipped in the solvent to start the chromatogram. The spots are detected either by prolonged (0.5 hr.) irradiation with u.v. light, which leads to the appearance of a blue fluorescence, augmentation of the photographic opacity of the spot and an increase in its reducing power, or by exposing the paper to Cl_2O gas for 2 hr. and, after keeping it in air for 24 to 48 hr., spraying with 5 per cent. KI and then with starch solution.

E. J. H. BIRCH

2859. The microchemical identification of β -phenylisopropylamine [amphetamine]. G. Cavicchi Sandri (Inst. of Chem. Pharmacy, Univ. of Ferrara, Italy). *Mikrochim. Acta*, 1956, (1-3), 244-251.—The application of a special potassium bismuth iodide solution for the microchemical detection of amphetamine (I) and its differentiation from N-methylamphetamine (II) is proposed. I produces two compounds, each with characteristic crystal forms and corresponding respectively to $\text{BiI}_3 \cdot 2\text{H}_2\text{C}_6\text{H}_5\text{N}$ and $\text{BiI}_3 \cdot \text{HIC}_6\text{H}_5\text{N} \cdot 4\text{H}_2\text{O}$. II produces with the reagent only one compound, $\text{BiI}_3 \cdot \text{HIC}_{10}\text{H}_{13}\text{N} \cdot 2\text{H}_2\text{O}$, characterised by an entirely different crystal formation. An additional differentiation between I and II is made possible by treatment with bromobismuthic acid. With this reagent I produces characteristic crystals corresponding to $\text{BiBr}_3 \cdot 3\text{HBr} \cdot 3\text{C}_6\text{H}_5\text{N} \cdot 3\text{H}_2\text{O}$, whilst II gives no reaction.

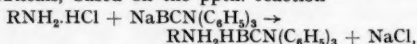
D. F. PHILLIPS

2860. Microchemical and microphysical testing possibilities on medicinally important pyridine derivatives. F. Lüdy-Tenger (Burgdorf, Switzerland). *Mikrochim. Acta*, 1956, (1-3), 104-117.—Precise directions are given for distinguishing the following pyridine derivatives—nicotinamide, nicotinic acid, isonicotinic acid, isoniazid, nicotinic acid hydrazide (as contaminant of isoniazid)—with one drop of "Bi I 1.5" (bismuth carbonate, 0.5; conc. HCl, 1.5; KIO_3 , 4.0; H_2O to 10 ml). The test is not completely satisfactory with isoniazid and a more satisfactory differentiation was sought through the reaction of aldehydes and ketones with a terminal NH_2 group. The products from a large number of aldehydes were examined, but those from benzaldehyde and vanillin are the only ones recommended because they are distinctive and may be easily obtained. By using the Leitz-Jelley microrefractometer, a calibration curve was prepared enabling quant. determination of nikethamide to be carried out.

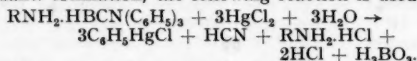
D. F. PHILLIPS

2861. The qualitative and quantitative estimation of nitrogen-containing pharmaceuticals with "Casignost" (sodium triphenylcyanoboron). O.-E.

Schultz and H. Goerner (Pharm. Chem. Inst., Univ. Tübingen, Germany). *Arch. Pharm., Berlin*, 1955, **288**, 520-525.—Procedures in which Na triphenylcyanoboron (**I**) are used are described for the qual. determination of a number of pharmaceuticals, based on the pptn. reaction—



in the presence of a 2.7 per cent. AlCl_3 soln. For the quant. estimation, the following reaction is used—



A 5-ml aq. test soln. containing 3 mg of the compound is treated with three drops of a 0.2 N AlCl_3 soln., followed by three drops of a 1 per cent. acetic acid soln. and, after mixing, 0.5 ml of a 3 per cent. soln. of **I** is added, shaken, and set aside for 2 to 3 hr., when the resulting ppt. is filtered off. After washing with a soln. of **I** (1 ml of **I** dissolved in 1 ml of acetone, and 0.4 ml of this soln. removed and diluted to 100 ml), and a final aq. washing, the ppt. is dissolved in 1 ml of acetone and treated with 1 ml of a satd. aq. soln. of HgCl_2 and 20 ml of water. The soln. is then titrated with 0.01 N NaOH, with methyl red as indicator. The soln. is boiled, and a 20 per cent. KI soln. (1 ml) is added dropwise until the HgCl_2 is pptd.; then 0.01 N HCl is added until the soln. is acid, and boiling is repeated to expel HCN and CO_2 . The cooled soln. is finally back-titrated with 0.01 N NaOH. Blank estimations are required.

G. R. WHALLEY

2862. Identification of saccharin according to Klostermann and Scholta. T. Brouwer (Public Analyst's Lab., 's Gravenhage, Holland). *Chem. Weekbl.*, 1956, **52** (12), 184-186.—The method of Klostermann and Scholta (*Z. Untersuch. Nahr.-u. Genussm.*, 1916, **31**, 67), consisting in the conversion of saccharin into phenol red, is modified as follows. Extract the saccharin from the sample by a suitable solvent and boil for at least 15 min. in 10 per cent. HCl; allow to evaporate to dryness in a dish, cool, and moisten with a trace of water by means of a glass rod. Add about 10 g of phenol, mix, and carefully add some P_2O_5 ; cover the dish with a watch-glass and heat in an oven at 100°C for 10 min. An orange colour indicates that saccharin is present. After cooling, add water and make alkaline; a red-purple colour develops. This should persist on the addition of $(\text{NH}_4)_2\text{S}$. Interference from vanillin is avoided by oxidation with KMnO_4 . The method is claimed to be sensitive to 0.01 g of saccharin.

H. A. FISHER

2863. [Toxicological] identification and determination of mercury in biological materials. H. Wanntorp and A. Dyfverman (State Vet. Med. Inst., Stockholm, Sweden). *Ark. Kemi*, 1956, **9** (1), 7-27.—By using the dithizone-EDTA method, modified for the determination of Hg, e.g., in body tissues in cases of suspected poisoning, 10 to 100 μg of Hg in 25 g of muscle, kidney, liver, etc., could be determined with a mean recovery of 97 per cent. Extensive data are presented with CCl_4 or CHCl_3 as solvent. By measurement of the colour intensity of the dithizone solution at a suitable wavelength after shaking with a test solution under known conditions, certain metals which produce complex dithizone compounds can be quant. determined. Silver and copper interfered markedly with the extraction; the effect of copper was studied further.

Details are given for the micro-determination of Hg in amounts $<0.1 \mu\text{g}$ after the mercury has been obtained in metallic form, based on the method of Stock *et al.*, and of the qual. test on the dithizone solution used in the quant. determination.

S.C.I. ABSTR.

2864. Compleximetric determination of zinc, mercury, lead, aluminium and bismuth in pharmaceutical preparations. J. S. Faber (Pharmaceutical Dept., Groningen Univ., Holland). *Pharm. Weekbl.*, 1956, **91** (6), 177-189.—The previously described compleximetric methods (*cf. Anal. Abstr.*, 1956, **3**, 2423) have been extended to these metals. Particular reference is made to the use of catechol violet as indicator in the titration of Al and Bi. Detailed methods, which are claimed to be equally accurate but more convenient than established procedures, are given for most pharmaceutical preparations containing Zn, Hg, Pb, Al and Bi.

H. A. FISHER

See also Abstracts 2671, 2794, 2810, 2811, 2812, 2884.

Food

2865. Sucrose loss from ice-cream on storage. H. J. Evans, W. Kwantes, D. C. Jenkins and J. I. Phillips (Public Analyst's Lab., Carmarthen, Gt. Britain). *Analyst*, 1956, **81**, 204-210.—Loss of sucrose frequently occurs in ice-cream stored even at the temp. of the domestic refrigerator ($\approx 36^\circ\text{F}$). The quoted results of an investigation show that the lost sucrose is replaced only partly by reducing sugars, and qual. tests suggest the presence of the long-chain saccharide dextran. In a bacteriological examination of stored samples showing loss of sucrose, *Leuconostoc mesenteroides* was isolated on a sucrose-nutrient agar medium. The ability of the isolated organism to produce dextran in sucrose soln. and to cause reduction of the sucrose content of ice-cream was confirmed. *Ln. mesenteroides* survives pasteurisation and so may be derived from the ingredients of the original mix or from outside contamination. A few expts. suggested that ice-cream may be stored without change in "deep freeze." Since ice-cream must contain <7.5 per cent. of sucrose [The Food Standards (Ice Cream) Order, 1953], determination of sucrose should be made preferably while the sample is still frozen solid and certainly within a few hours of its storage at room temp.

A. O. JONES

2866. A quick method for assessing the suitability of starches for acid hydrolysis. S. Winkler (Starch Ind. Res. Inst., Berlin). *Stärke*, 1955, **7** (9), 226-233.—The use of sealed glass tubes in place of autoclaves for laboratory testing of starches is claimed to have the following advantages: elimination of the influence of the material of the autoclave; possibility of running a number of experiments simultaneously, thus eliminating the differences of temperature and speed of heating and cooling; and greater ease in following visible changes during hydrolysis. A standard concentration of 4 g of starch (dry weight) in 10 g of soln. is used; the glass tubes have an inside diameter of 13 mm, and a wall thickness of 8 mm. The quality of the glass does not influence the results. Heating is by means of a glycerol bath to temperatures up to 160°C . The

tubes are placed in the bath in a horizontal position and slowly rotated by means of a special device, which is described. The degree of hydrolysis is determined by standard methods. Optical activity was found to be an inaccurate measure of hydrolysis. A quantitative relation between hydrolysis and optical activity does exist, but this varies with the type of starch.

H. A. FISHER

2867. The monomolecular surface film method for determining small quantities of yolk or fat in egg albumin. D. H. Bergquist and F. Wells. *Food Tech., Champaign*, 1956, **10** (1), 48-50.—The method of Heinemann and Rohr for determining micro quantities of fat in skim milk has been adapted for determining small quantities of yolk or fat in egg white. In this method, fat is extracted by using a combination of ether and light petroleum; an aliquot of the fat redissolved in light petroleum is spread as a monolayer on the surface of an acetic acid soln. The area of the spread is a measure of the quantity of yolk present. The spreading coefficient of egg fat was determined and the method was shown to give good recovery of egg fat from egg white, even after holding samples for extended periods at both 35° F and -10° F.

BRIT. BAKING IND. RES. ASS. ABSTR.

2868. Applying Hillig's rapid method for water-insoluble acids to fresh milk. T. R. Freeman and W. F. Lewallen (Kentucky Agric. Expt. Sta., Lexington, U.S.A.). *J. Dairy Sci.*, 1956, **39** (2), 219-220.—Variable results obtained on cream freshly separated from fresh raw milk when water-insoluble acids are determined by Hillig's method (*J. Ass. Off. Agric. Chem.*, 1953, **36**, 1077) are attributed to lipase activity during the mechanical separation of the milk and during the analytical procedure. It is considered that samples of fresh milk for assay should be heated at 160° F for 30 min., and that the results for water-insoluble acids on samples so treated are a true measure of their concentration in the freshly drawn milk.

W. H. C. SHAW

2869. The microchemical determination of iodine in milk and milk products. H. Hänni (Eidgenöss. Milchwirtschaft. Versuchsanstalt Liebefeld, Bern, Switzerland). *Mikrochim. Acta*, 1956, (1-3), 257-262.—The methods available for the determination of small amounts of iodine have mostly been worked out for blood and involve numerous difficulties when applied to substances containing both fat and albumin. A method is described in which pre-treatment of the sample with a mixture of equal parts of Na_2CO_3 and K_2CO_3 at a relatively low temp. is followed by incineration with acid KMnO_4 soln. The iodine in the ash is liberated by reduction with phosphorous acid and subsequently distilled. The iodine is determined either by the volumetric method of Zacherl and Stöckl with the Gorbach microburette (*Mikrochem.*, 1951, **38**, 278) or by an absorptiometric procedure in which the liberated iodine transforms an equivalent amount of hydroxylamine into nitrite. This is colorimetrically determined by the reaction with sulphanilic acid and 1-naphthylamine. No results are quoted nor does the author indicate accuracy or precision.

D. F. PHILLIPS

2870. The determination of milk solids-not-fat in ice-cream. B. Crowhurst (10 Lewes Road, Finchley, London). *Analyst*, 1956, **81**, 123-124.—The method described is based on the formal titra-

tion of milk proteins (Richmond, "Dairy Chemistry," 3rd Ed., Chas. Griffin & Co. Ltd., London, 1920, p. 182). The sample (10 g) is titrated to the phenolphthalein end-point with 0.1 N NaOH, 3 ml of 40 per cent. formaldehyde soln. are added, the mixture is stirred and the titration is continued. The result is corrected by the titre of 3 ml of the formaldehyde. The difference between the two titrations of the sample ($x - y$) is multiplied by 10 to obtain the aldehyde figure. The percentage of milk protein is $(x - y) \times 10 \times 0.17$, and since skimmed-milk powder contains 30 per cent. of milk protein then $(x - y) \times 5.67$ is the percentage of milk solids-not-fat in the sample. The presence of wheat flour, gelatin and the emulsifiers and stabilisers commonly used in ice-cream does not affect the determination.

A. O. JONES

2871. The vitamin-A and carotene potency of national (household) butter determined by a chromatographic-ultra-violet spectrophotometric method of assay. W. G. Scott and R. J. Taylor (Gov. Lab., Clement's Inn Passage, London). *Analyst*, 1956, **81**, 117-121.—The method of Boldingh *et al.* (*Brit. Abstr. C*, 1951, 267) for the determination of vitamin A and carotene in margarine is applicable, with slight modification, to the determination of these in butter. The modified method is that of the official assay of margarine (*Statutory Instrument*, 1954, No. 613). It was applied to the examination of 106 samples of imported butters and 10 samples of English butters in two laboratories, and the results obtained are tabulated. The mean vitamin-A and carotene potencies for the 116 samples examined were 23.6 and 9.5 i.u. per g. respectively.

A. O. JONES

2872. The identification of fat-soluble synthetic dyes and annatto in margarine. F. Hoeke and H. Onrust (Public Analyst's Lab., Rotterdam, Holland). *Chem. Weekbl.*, 1956, **52** (12), 186-187.—The use of synthetic dyes in margarine has been prohibited in Holland since January 19th, 1956. The following method for their identification is described. Melt ≈ 20 g of margarine in a 50-ml conical flask, add 1 g of tragacanth powder, mix well and filter by suction. Dissolve ≈ 10 g of the filtrate in 50 ml of light petroleum (boiling range, 40° to 60° C) and shake well with 5 g of Al_2O_3 (calcined); allow to settle, decant the supernatant fluid and wash the Al_2O_3 with 4×25 ml of light petroleum by decantation. Dry the Al_2O_3 at room temperature or with gentle heat, add 50 ml of 96 per cent. alcohol, shake well, and filter by suction. An uncoloured filtrate indicates the absence of synthetic dyes. If yellow, the filtrate is divided into two portions; one is treated with 3 ml of SnCl_4 solution and the depth of colour is compared with the untreated portion after 1 hr. Fading indicates the presence of synthetic dyes. Annatto is adsorbed on the Al_2O_3 and may be detected by the H_2SO_4 colour test.

H. A. FISHER

2873. Determination of water by nuclear magnetic absorption in potato and apple tissue. T. M. Shaw and R. H. Elsen (U.S. Dept. of Agric., Albany, Calif., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (2), 162-164.—The application of the quant. measurement of hydrogen in liquids by nuclear magnetic resonance (Shaw and Elsen, *Anal. Chem.*, 1955, **27**, 1983) to the determination of the water content of fruit and vegetable tissues has been investigated with cylinders of potato and apple tissue. With 12 samples of potato the results show a standard

deviation of ± 3 per cent. and agree generally with those obtained by vacuum-oven drying. Error is shown to arise from the non-uniform distribution of water in the potato tissue; hence average readings should be taken from four different orientations of the sample cylinder. This results in a standard deviation of less than ± 2 per cent. Under the same conditions, apple tissue shows a standard deviation of ± 7.7 per cent. In this case it is concluded that soluble sugars are responsible. After the application of a correction the standard deviation is only ± 1.3 per cent. H. B. HEATH

2874. Rapid colorimetric methods for simultaneous determination of total reducing sugars and fructose in citrus juices. S. V. Ting (Florida Citrus Exp. Sta., Lake Alfred, Fla., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (3), 263-266.—Ferricyanide is used in a carbonate-phosphate buffer as the oxidising agent for sugars, and the ferrocyanide produced is measured colorimetrically, with the blue solution formed after the addition of Nelson's molybdoarsenate reagent. When heated at 100°C for 10 min., glucose and fructose are oxidised in equal amounts; when heated at 55°C for 30 min., all the fructose, but only one-eighth to one-ninth of the glucose, is oxidised. The amounts of the two sugars can then be calculated. Results obtained by this method for reducing and total sugars in orange juices are compared with those of duplicate determinations in which the Shaffer-Hartmann volumetric method was used. S.C.I. ABSTR.

2875. Methods of colour measurement of wort and beer. H. Schilfarth (Versuchs- und Lehranstalt für Brauerei, Berlin). *Brauerei*, 1956, (4), 39-42.—The main advantages of the European Brewing Convention (E.B.C.) method over the older methods are: (i) increased accuracy, (ii) the use of permanent glass colour standards, (iii) ease of manipulation, and the fact that it standardises colour measurement in the European brewing field. As this method is visual, an allowance must be made for a measuring error of ± 0.5 E.B.C. unit. To overcome this error, work is being carried out with spectrophotometric methods. The colour of wort and turbid beer can be determined after centrifuging and filtration. Differences between E.B.C. values and those determined spectrophotometrically can be attributed to the fact that with the spectrophotometer only the yellow content is measured, whilst the E.B.C. method measures both the yellow and red contents. G. H. BAKER

2876. Direct photometric estimation of iron in wines with ferron. J. Roubert (École Nat. d'Agric., Algiers, Algeria). *Chim. Anal.*, 1956, **38** (4), 134-137.—Both Fe^{II} and total Fe can be determined with ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid), so that it is possible to express results in terms of Fe^{II} and Fe^{III} . None of the other constituents to be found in wines causes interference under the conditions of the estimation, since even the citrate and phosphate complexes of Fe^{III} are decomposed on warming to give the ferron complex. The slight interference shown by ethanol is overcome by the addition of 1 ml of ethanol to both sample and standard soln. *Procedure*—The sample (1 ml) is mixed with 4 ml of buffer soln. (8.85 ml of 0.2 N HCl made up to 100 ml with an 0.05 N soln. of K H phthalate) (pH 3), 1 ml of 95 per cent. ethanol and 1 ml of ferron reagent (0.2 per cent. aq. soln.). The soln. is warmed for 2 min. without boiling, then cooled, and after 3 min. the extinction is

measured at 610 m μ in a 1-cm cell against that of a blank prepared as above but with the ferron reagent replaced by H_2O . For the estimation of total Fe, 100 to 150 mg of $\text{K}_2\text{S}_2\text{O}_8$ are added to both sample and blank before warming. Calibration curves are prepared by using 1-ml portions of standard Fe^{III} soln. saturated with K H tartrate, containing up to 30 mg of Fe per litre. The method is rapid, a time of 15 min. being claimed for a duplicate determination of Fe^{II} and total Fe. The precision is within ± 1 mg per litre for <30 mg of Fe per litre. J. H. WATON

2877. Identification and determination of vitamin-P factors in several fermented beverages. J. Masquelier (Lab. de Zoologie et Parasitologie, 3 Place de la Victoire, Bordeaux). *Bull. Soc. Chim. Biol.*, 1956, **38** (1), 65-70.—The leucoanthocyanin and flavone fractions of vitamin-P factors are separated from wines, beer and cider and estimated. *Procedure*—After the alcohol has been distilled off, the sample is saturated with NaCl to precipitate tannins, and extracted with butanol after acidification. The butanol solution is diluted with 4 vol. of ether and the leucoanthocyanin fraction is extracted from it with 2 per cent. HCl, and the flavone fraction with 1 per cent. aq. Na_2CO_3 . The leucoanthocyanin fraction is heated to 50°C under reduced pressure to remove ether, and made up to 100 ml with water. Samples of various sizes are heated with HCl and the colour (stabilised with alcohol) is measured, leucoanthocyanidin prepared from *Pinus maritima* being used as a standard. The flavone derivatives are largely present as glycosides and these are hydrolysed by heating the fraction under reflux for 45 min. with 10 per cent. HCl. The aglycones are then extracted with ether, evaporated, washed with benzene, taken up in alcohol, evaporated in a tared capsule, and weighed. Dry white wines and cider contain 10 to 300 mg per litre of both factors, and sweet white wines and beers contain only flavone factors. E. J. H. BIRCH

2878. Rapid estimation of the oil content of oilseeds. A. R. S. Kartha and A. S. Sethi (Indian Agric. Res. Inst., New Delhi). *J. Sci. Ind. Res.*, B, 1956, **15** (2), 102-103.—The sample of oilseed (0.1 to 0.3 g) is ground with ≈ 2 g each of anhyd. Na_2SO_4 and glass powder, then packed into a small glass percolator over a $\frac{1}{4}$ -in. layer of anhyd. Na_2SO_4 and light petroleum (boiling range 70° to 90°C) is percolated through. Most of the oil from the sample is contained in the first 7 to 8 ml, only a negligible quantity being contained in the next 3 to 4 ml. The light petroleum is driven off by heating the percolate in an air-oven at 100°C . By placing four filter-paper strips (1 sq. in.) in the dish, the time of evaporating off the light petroleum was shortened from between 2 and 3 hr. to between 20 and 30 min. When the iodine value or free toopherol content of the oil is to be determined, the extraction is made with 25 to 30 ml of ether, and no filter-paper strips are used. S.C.I. ABSTR.

2879. Applications of ultra-violet spectrophotometry to the analysis of fats. II. A. Vázquez Roncero. *Grasas y Aceites*, 1955, **6** (6), 290-297.—The determination of small and of large proportions of conjugated fatty acids in oils by u.v. spectrophotometry is described, and the complications arising from the presence of different *cis-trans* isomers are indicated. Non-conjugated acids are converted into conjugated acids by alkali-isomerisation for spectrophotometric analysis, and the three

conditions for isomerisation in main use, namely, the use of 6.5 per cent. KOH in ethanediol at 180° C for 25 min., 11 per cent. KOH in glycerol at 180° C for 45 min., and 21 per cent. KOH in ethanediol at 180° C for 15 min., are compared.

L. A. O'NEILL

2880. Characteristics of Brazilian lards and methods of analysis. A. Lacerda (Bromatology Lab., Rio de Janeiro). *Arquiv. de Bromatologia*, 1955, **3** (1), 5-17.—Standard Brazilian methods for the analysis of lards are outlined and results for 58 samples are reported. For the determination of iodine values, a variation of the Hübl method is preferred; the iodine soln. is added to a soln. of the lard in CHCl_3 , followed by the HgCl_2 soln., and a reaction time of 2 hr. is allowed.

L. A. O'NEILL

2881. Direct estimation of saturated acids in small amounts of fats or mixed fatty acids. A. S. Sethi and A. R. S. Kartha (Indian Agric. Res. Inst., New Delhi). *J. Sci. Ind. Res.*, B, 1956, **15** (2), 103-105.—Seven fats (5-g and 1-g samples) were oxidised by the acetic acid - acetone - permanganate procedure and the products of oxidation were isolated and hydrolysed with KOH. Excess of KOH was neutralised with dil. H_2SO_4 and the pptd. acids were redissolved in aq. NH_3 before applying the Bertram separation. Results indicated very little difference in the yield of saturated acids from 1-g and 5-g samples under the experimental conditions specified. The loss of saturated acids of higher mol. wt. during estimation by the Bertram method is therefore negligible. Data are presented and techniques are discussed.

S.C.I. ABSTR.

2882. Identification [of driers] in drying oils. S. R. Ramachandran and R. S. Prayag. *Paint India*, 1955, **5** (7), 33-37.—Conjugated drying oils containing different driers and drier combinations when impregnated on to paper and stoved under defined conditions (100° C for 5 min.) produce patterns characteristic of the metals (Co, Mn, Pb, Zn or Cu) of the drier system (but independent of the acid radicle of the driers); these assist in the identification of the drier metal. Typical photographs of patterns (which are not produced in the absence of driers) are shown.

L. A. O'NEILL

2883. New method of microbiological determination of nicotinamide. J. Claveau. *Ind. Agric. Aliment.*, 1956, **73** (1), 3-10.—It is shown that the rate of growth of *Saccharomyces lactis* β is precisely related to the concn. of nicotinamide present in the medium (up to a concn. of 2.5 μg per 50 ml), and methods are developed with this test organism to determine nicotinamide in cheese and other milk products. One method is based on the electro-photometric measurement of turbidity to give the growth-rate of the organism; a second method is based on measuring the rate of fermentation to the amount of alcohol produced. In each case, comparisons are made with standards of known nicotinamide content.

S.C.I. ABSTR.

2884. The estimation of vitamin B₁₂. Vitamin-B₁₂ Panel of the Analytical Methods Committee of The Society for Analytical Chemistry (20 Eastcheap, London). *Analyst*, 1956, **81**, 132-136.—The Panel accepted published evidence of the non-specificity of microbiological assays of vitamin B₁₂ with *Bacillus*

coli, *Lactobacillus leichmannii*, or *Euglena*. A more specific technique with *Ochromonas malhamensis* was studied and subjected to collaborative tests, with satisfactory results. The details of the recommended procedure, based on that of Ford (*Brit. Abstr. C*, 1953, 27) with a modified extraction procedure, are given.

A. O. JONES

See also Abstract 2725.

Sanitation

2885. The determination of dissolved oxygen in water containing reducing substances. I. Davies, M. N. Redfearn and D. E. Y. Remer (Battersea Generating Station, Kirtling St., London). *Analyst*, 1956, **81**, 113-116.—The effect of interfering substances on the Winkler method for determining dissolved O in water is shown experimentally. Fe^{III} and Cu^{II} are relatively harmless, but Fe^{II} , Cu^I , SO_3^{2-} and S^{2-} all give rise to an apparent loss of dissolved O. The disadvantages of certain methods designed to overcome this difficulty are discussed, and a system of ion-exchange columns is proposed by which the interference is removed while the sample is being taken. In the method finally adopted, the first column is a 15-cm column (diam. 2.5 cm) of Amberlite IRA-400(OH) resin that has been converted to the (MnO_4^-) form by soaking in 2 per cent. KMnO_4 soln. and washing free from KMnO_4 (an "oxite" column). With this column, complete oxidation of dil. soln. of Fe^{II} and SO_3^{2-} can be effected. The effluent is then passed through a second column (60 cm \times 4 cm) containing a mixture of De-Acidite FF and Zeo-Karb 225. Results show that this system effectively removes the interfering substances, and the Winkler test can then be applied without modification. It fails when much sulphide is present.

A. O. JONES

2886. The determination of lead in water. I. N. Sosunova. *Inform.-Metod. Materialy. Gos. Nauch. Issledovatel. Sanit. Inst.*, 1954, (5), 32-35; *Ref. Zhur., Khim.*, 1955, (17), Abstr. No. 37,516.—Pour the sample (100 ml) into a cylinder with a ground glass stopper, add 4 ml of 25 per cent. NH_4Cl soln., 1 ml of 1 per cent. CaCl_2 soln., 10 ml of 25 per cent. aq. NH_3 soln., and 1 ml of 1 per cent. Na_2CO_3 soln. Insert the stopper and shake, then allow to stand for 24 hr. At the same time treat 100 ml of twice-distilled H_2O similarly for use as a blank. Coloured waters are boiled before pptn., adding 5 ml of 5 per cent. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ soln. and 50 ml of distilled H_2O to 100 ml of the sample, and evaporating down to 100 ml. The following day, separate the ppt. from the clear liquid (used for determination of Cu) and wash with 3 ml of aq. NH_3 soln. (5 ml of 25 per cent. aq. NH_3 made up to 100 ml), remove the wash liquor and centrifuge out the ppt. Pour off the liquid, add 2 ml of 2 per cent. HCl to the ppt., transfer to the cylinder in which pptn. took place, washing out the centrifuge tube twice. The ppt. dissolves completely in the HCl . Transfer the soln. to a 10-ml colorimeter tube and make up to the mark. Then add 1 ml of 50 per cent. K Na tartrate soln., 1 ml of 30 per cent. NaOH soln., and 0.1 ml of 15 per cent. $\text{Na}_2\text{S}_2\text{O}_4$ soln. (aq. or in glycerol), and mix. A yellow-brown colloidal suspension of PbS is formed, which is compared with permanent painted standards or with freshly prepared liquid standards containing 0 to 300 μg of $\text{Pb}(\text{NO}_3)_2$ per litre. The accuracy of the method is within ± 20 per cent.

C. D. KOPKIN

2887. Detection of petroleum products in natural waters by means of fluorescence. B. Nietsch (Hygien.-bakteriol. Untersuchungsanstalt, Vienna). *Mikrochim. Acta*, 1956, (1-3), 171-178.—The importance of obtaining information on the contamination of natural waters by petroleum products is discussed. A method is described by which down to 1 μ g of petroleum products per litre may be detected by measurement of their fluorescence in u.v. light. Shake the sample with ≈ 10 mg of MgO per 100 ml and filter. The MgO absorbs the oil. Spread the filter-paper on a clock-glass and examine under u.v. light (a blank determination is treated similarly). Test the filtrate for complete removal of the oil traces under u.v. light. Alternatively, shake the sample with light petroleum and examine the extract in u.v. light. D. F. PHILLIPS

2888. The detection and determination of traces of polynuclear hydrocarbons in industrial effluents and sewage. IV. The quantitative examination of effluents. P. Wedgwood and R. L. Cooper [The St. Albans Lab., Eastern Gas Board (Watford Div.), Clarendon Rd., Watford, England]. *Analyst*, 1956, **81**, 42-44.—Sewage-works effluent (1 litre) is extracted three times with chloroform, the solvent is carefully removed by evaporation and the residue is dissolved in a few ml of cyclohexane and run through a short alumina column (1 cm \times 1 cm). Each eluate is examined for specific hydrocarbons, made up to a suitable vol. and the extinction is measured. The lower limit of the determination of pyrene in 1 litre of effluent is ≈ 0.0001 p.p.m. and the quoted results indicate generally a concn. of ≈ 0.001 p.p.m., with a reduction from inlet to outfall. For carburetted water-gas plant effluent the chloroform extract of the acidified liquid (10 to 100 ml) is transferred into cyclohexane and the soln. is run through an alumina column (6 to 10 cm \times 1 cm). The hydrocarbons separate into between 10 and 40 eluates which are examined and suitably combined for determination. Typical results are quoted. For spent ammoniacal liquor, 100 to 200 ml are made strongly alkaline and are extracted repeatedly with chloroform as previously described (*Anal. Abstr.* 1956, **3**, 575). Subsequent procedure is as for carburetted water-gas plant effluent. The pyrene content is of the order of 0.01 p.p.m. A. O. JONES

2889. Analytical determination of trace constituents in metal-finishing effluents. IX. Determination of free chlorine in effluents. E. J. Serfass, R. F. Muraca and D. G. Gardner. *Plating*, 1955, **42** (4), 401-402.—A colorimetric method is described for the determination of 5 to 50 p.p.m. of Cl in effluents in the presence of > 1000 p.p.m. each of Na, K, Ca, Al, Mg, SO_4^{2-} , Cl^- and NO_3^- ; > 50 p.p.m. each of Zn, As, Sb, Bi, Ni, Cu, PO_4^{3-} , Cd, Cr^{III} , Co, Pb, Ba, Ag and Hg; > 10 p.p.m. of Fe^{III} ; > 5 p.p.m. of NO_2^- ; and 0.5 p.p.m. of Mn^{III} . A 10-ml aliquot of effluent is diluted to 500 ml (with Cl-free water), 10 ml of the diluted effluent are added to the sample tube of the comparator and 0.5 ml of o-tolidine is added. The intensity of the colour developed after < 10 min. is matched with permanent standards. METALL. ABSTR.

2890. The photocolorimetric determination of the arsenic and phosphorus contents in effluents from metallurgical plants. L. N. Kushakovskii and T. D. Posdnyakova. *Gigiena i Sanit.*, 1955, (4), 46-48; *Ref. Zhur., Khim.*, 1955, (19), Abstr. No. 43,241.—In one portion of the liquid to be analysed,

the content of P is determined by formation of the molybdophosphate complex and reduction by a specially prepared solution of aminonaphthol-sulphonic acid. In another portion of the liquid, the content of As plus P is determined by reduction with freshly prepared SnCl_2 solution. The formation of the molybdenum complex is carried out in acid medium at room temp. The difference in the results gives the content of As. C. D. KOPKIN

2891. Determination of small amounts of dianisidine in the air of factories. A. I. Bul'ycheva and P. I. Mel'nikova. *Khim. Prom.*, 1955, (1), 50-52; *Ref. Zhur., Khim.*, 1955, Abstr. No. 46,267.—The sample (100 to 200 litres) of air is passed at the rate of 20 litres per min. through a tube containing cotton wool moistened with 1 ml of water or through a glass filter. The absorbed dianisidine is washed out with several 2 to 3-ml portions of water giving 10 to 15 ml in all. Two or three such extracts are obtained. A test is made on 2 ml by one of the following methods: (i) reaction with 0.1 ml of 1 per cent. HCl soln. plus 0.1 ml of 1 per cent. NaNO_2 soln., followed after 3 min. by the addition of 0.1 ml of 0.1 per cent. NaOH soln. and 0.1 ml of 0.2 per cent. 8-amino-1-naphthol-5:7-disulphonic acid in a 5 per cent. NaHCO_3 soln., giving a pale to deep-blue colour stable for 2 hr., (ii) reaction with 0.2 ml of 1 per cent. FeCl_3 soln., giving a yellow to orange colour in 4 to 5 min., stable for 1.5 hr., (iii) reaction with 0.2 ml of 1.5 per cent. aniline hydrochloride soln. and 0.1 ml of 1 per cent. FeCl_3 soln., giving a colour stable for 1.5 hr., or (iv) reaction with 0.5 ml of 10 per cent. HCl soln. and 0.5 ml of 5 per cent. $\text{K}_3\text{Fe}(\text{CN})_6$ soln., giving a greenish-yellow to orange colour stable for 3 hr. The methods are suitable for detecting 0.002 to 0.05 mg of dianisidine in 2 ml, and benzidine in amounts of 0.002 to 0.1 mg does not interfere. The colours are compared visually or photometrically against a freshly prepared series of standards. G. S. SMITH

2892. Identification of ozone in the Los Angeles atmosphere. F. E. Littman and C. W. Marynowski (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 819-825.—In the technique described, silica gel is used at the temp. of liquid oxygen to concentrate the atmospheric ozone. The adsorbed gases are flushed into an optical cell and their u.v. spectra are compared with those of synthetic mixtures of oxygen and ozone. By this method, 30 to 45 per cent. of the total oxidant in the Los Angeles atmosphere was identified as ozone. K. A. PROCTOR

See also Abstracts 2635, 2654, 2725, 2862, 2926.

Agriculture and Plant Biochemistry

2893. The determination of calcium in plant material by flame photometry. R. G. Hemingway (Agric. Chem. Dept., The University, Glasgow, Gt. Britain). *Analyst*, 1956, **81**, 164-168.—Owing to interference from PO_4^{3-} the EEL flame photometer cannot be used for the direct determination of Ca in plant-ash extracts. In the method described, PO_4^{3-} are separated from the soln. by means of a column of the cation-exchange resin Amberlite IR-120(H). A mixture of the ash and HCl is evaporated, leached with hot water, and filtered, and the vol. is adjusted to 100 ml. An aliquot portion is applied to the column, which is then washed with water. The Ca is eluted with 5 N HNO_3

and determined by the flame photometer. No interference is given by Al, Fe, Mn, Mg, K and Na in the amounts likely to be found in plant material. The accuracy is within ± 2.2 per cent.

A. O. JONES

2894. The determination of calcium and magnesium in plant material with disodium ethylenediaminetetra-acetate. A. M. Smith and E. S. R. McCallum (Edinburgh and East of Scotland College of Agric., Edinburgh, Gt. Britain). *Analyst*, 1956, **81**, 160-163.—In the method developed, interferences by Fe, Mn, PO_4^{3-} and NH_4Cl are overcome. The ignited material is freed from SiO_2 and dissolved in HCl. An excess of 10 per cent. FeCl_3 soln. is added and the pH is adjusted with aq. NH_3 soln. and acetic acid to the red end-point of methyl red, used externally. The mixture is filtered quickly at the boiling point (filtrate a), the ppt. is dissolved in 2 N HCl and the pptn. and filtration are repeated (filtrate b). Manganese is removed from filtrate a, which is then combined with b; the liquid is made just acid to methyl red and the vol. is adjusted to 250 ml. A 20-ml aliquot is diluted with 30 ml of water, 3 ml of an NH_4Cl -aq. NH_3 buffer soln. are added and the soln. is titrated for Ca and Mg with 0.018 N EDTA (disodium salt) to the blue end-point of Eriochrome black T. The NH_4Cl is removed by boiling with NaOH, the pH is adjusted to the acid point of methyl red and then to pH 12 by addition of 0.3 N NaOH, and is titrated for Ca alone with the EDTA soln. to the purple end-point of murexide. The method is accurate and rapid, but the number of samples that can be handled simultaneously is small.

A. O. JONES

2895. Micro-analytical detection of lignin. K. Kratzl (Timber Res. Inst., Vienna). *Mikrochim. Acta*, 1956, (1-3), 159-170.—In order to designate a material as lignin, information must be obtained from a number of techniques. These include botanical staining methods (wood staining and wood colour reactions) as well as physical and chemical procedures. Physico-chemical methods include u.v. and i.r. absorption. Information on the aromatic degradation products of lignin must be obtained through chemical studies. In many cases micro-chemical techniques offer the only possible approach to both scientific and technical problems. (41 references.)

D. F. PHILLIPS

2896. Estimation of amino acids in soil hydrolysates by the Moore and Stein method. F. J. Sowden (Canada Dept. Agric., Ottawa, Canada). *Soil Science*, 1955, **80**, 181-188.—Three different Canadian soils were examined. The soil (10 g) was hydrolysed by refluxing with 250 ml of 6 N HCl for 24 hr., the supernatant liquid was evaporated to dryness *in vacuo*, and the residue taken up in 10 ml of H_2O . The amino acids were adsorbed on Dowex resin and eluted first with pH 3.41 buffer and then with pH 4.25 buffer. The amount of amino acids in the fractions was determined colorimetrically by means of the Moore and Stein ninhydrin reagent (*cf. J. Biol. Chem.*, 1948, **176**, 367). Their identity was established by paper chromatography, with butanol-acetic acid-water (4:1:1) as developer. Separation of the amino acids obtained from soil by this method is only moderately good. Their distribution in the three soils is similar; tests for sulphur-containing amino acids were positive, though only very small amounts appear to be present.

H. A. FISHER

2897. Internal standards in arc excitation of soil and plant ash. A. C. Oertel. (Division of Soils, C.S.I.R.O., Adelaide). *Aust. J. Appl. Sci.*, 1955, **6** (4), 467-475.—A theoretical study of the increase in precision of measurement of line intensity obtainable by the use of an internal standard has shown that an internal standard is of real value only when the coeff. of correlation of the line pair is < 0.8 and when the individual errors of the two lines are approx. equal. A practical examination of the arc excitation of soil and plant ash has shown that precision may be increased when the line pair consists of corresponding lines of two elements that have very similar volatilisation curves. If such a line pair is not available, precision can be increased more efficiently by replication with no internal standard.

O. M. WHITTON

2898. Rapid determination of nitrogen, phosphorus and potassium in fertilisers. J. Solari. *Ind. Agric. Aliment.*, 1956, **73** (1), 25-27.—The determinations of free NH_3 by distillation, fixed N by the Kjeldahl method, K and P by the Bertrand method, P by the molybdophosphate colorimetric method, and K by pptn. with $\text{NaB}(\text{C}_2\text{H}_3\text{O}_4)_4$, are reviewed in relation to their application to natural and artificial fertilisers, from the standpoint of rapidity, simplicity and sufficient accuracy for the purpose.

S.C.I. ABSTR.

2899. The estimation of vitamin-B₁₂ activity in feeding-stuffs with *Lactobacillus leichmannii* and *Ochromonas malhamensis*. R. H. Shrimpton (Rowett Res. Inst., Bucksburn, Aberdeenshire, Gt. Britain). *Analyst*, 1956, **81**, 94-99.—A description is given of the microbiological methods for determining the vitamin-B₁₂ activity of some animal by-products used as feeding-stuffs. The feeding-stuffs assayed were herring meal, white-fish meal, whale-meat meal, meat and bone meal and dried skim milk. The growth of the organism in the medium was measured turbidimetrically in an EEL nephelometer. All but one (herring meal) of the feeding-stuffs showed different vitamin-B₁₂ activities for each of the test organisms. *O. malhamensis* appears to be no better than *L. leichmannii* for predicting the vitamin-B₁₂ activity of feeding-stuffs for chicks. A semi-automatic dispensing syringe is described and also a simple shaker for use in growing cultures of *O. malhamensis*.

A. O. JONES

2900. Modified method for the assay of arsenical insecticides. I. Paris green. M. R. Verma, V. M. Bhuchar and R. Dass (Nat. Phys. Lab., New Delhi, India). *Z. anal. Chem.*, 1956, **149** (6), 401-407.—In the analysis of Paris green (Cu acetoarsenite), interference in the determination of As_2O_3 due to Cu^{II} is overcome by complexing the Cu with K citrate before iodimetry of the As_2O_3 ; Cu is subsequently determined at pH 3 to 3.5. This method is applicable over wide ranges of composition and is more rapid than other procedures that have been used. The accuracy is within ± 1 per cent. on about 15 to 350 mg of CuO and 50 to 250 mg of As_2O_3 .

II. Iodimetric determination of copper, arsenate and arsenite. M. R. Verma, V. M. Bhuchar and R. Dass. *Ibid.*, 1956, **149** (6), 407-414.—The determination of arsenate in the presence of Cu and arsenite (*cf. Part I, above*) is made possible by the reduction of arsenate to arsenite, either by digestion with S - H_2SO_4 or by pptn. of CuI and reduction with red P and I; in each case the total As^{III} is then determined iodimetrically. Both methods are preferable to the normal distillation procedure.

Results on Paris green and Scheele's green show good agreement (within ± 2 per cent.) of As_2O_3 contents by the three methods. J. P. STERN

2901. Methods for determination of insecticide residues in plant material. I. Otter (Fisons Pest Control Ltd., Chesterford Park Res. Sta., Essex, England). *Mikrochim. Acta*, 1956, (1-3), 125-133.—The determination of the organophosphorus insecticides known as dimefox, schradan and mipafox is based on knowledge of the P content. Preliminary treatments for a range of plant materials on samples of from 25 to 100 g are described. This is followed by chloroform extraction and separation of the insecticide from any naturally occurring phosphorus compounds by vacuum micro-distillation. With dimefox the distillation is conducted in a mixture of glycerol and ethanediol in a specially designed apparatus to prevent losses. The P is finally determined colorimetrically. A limit of detection of 0.05 to 0.1 p.p.m. is attained. Recoveries are from 60 to 100 per cent. D. F. PHILLIPS

2902. Chemical detection of parathion (folidol) in organs of cadaver, by a diazotisation method combined with paper chromatography. Hiroyasu Hamada (Sch. Med., Tokushima Univ., Japan). *Shikoku Acta Medica*, 1955, 7 (6), 1-6.—Parathion (OO-diethyl O-p-nitrophenyl thiophosphate) (I) may be detected in organs from a dead body by the following method. Macerate 1 g of the organ (or 1 ml of blood or urine) with benzene (10 ml) for 24 hr. Reduce the vol. of liquid obtained to 1 ml on a steam bath and complete the evaporation to dryness at room temp. Dissolve the residue in ethanediol (2 ml). Add *N* HCl (1 to 1.5 ml) and zinc dust (0.3 to 0.5 g) and heat on a steam bath for 30 min. at 40° C; cool and filter. To the filtrate add HCl (10 per cent.) (5 drops) and NaNO_2 soln. (0.2 per cent.) (5 drops), shake for 5 min. and add urea soln. (25 per cent.) (5 drops). Set aside for 15 min., remove the excess of NO_2^- and add Tsuda's testing soln. (0.2 per cent.) (3 drops). A purple-red colour is formed within 40 min. if I is present. When subjected to ascending paper chromatography this coloured liquid shows an R_F of 0.96 to 0.97 when developed with ethanol-butanol-water (6:2:3). The method will detect I in a concn. of 1 in 10^6 even if the organ is decomposed. H. B. HEATH

2903. Spectrophotometrical detection of parathion (folidol) in organs of cadaver. Hiroyasu Hamada (Sch. Med., Tokushima Univ., Japan). *Shikoku Acta Medica*, 1956, 8 (1), 1-6.—The diazotisation method for the detection of parathion (I) (cf. *Anal. Abstr.*, 1956, 3, 2902) is further examined. The extinction of the resulting coloured soln. is measured at 560 μ . By this method I can be detected in a concn. of 1 in 4×10^6 . H. B. HEATH

2904. Determining traces of octamethylpyrophosphoramide (schradan) in crops. D. F. Heath, J. Cleugh, I. K. H. Otter and P. O. Park (Fisons Pest Control, Ltd., Chesterford Park Res. Sta., Essex, England). *J. Agric. Food Chem.*, 1956, 4 (3), 230-233.—The schradan-treated crop samples (50 g) are macerated with water (50 ml), followed by filtration or centrifugation, and extraction of the aq. macerate at pH 8 to 10 (*N* NaOH) with two equal vol. of chloroform. The solution is clarified and concentrated to ≈ 25 ml and transferred to a micro-distillation apparatus, a modification of that of Klein and Werner. The chloroform is evaporated,

and the residue is heated under reduced pressure (1 mm of Hg). The convective air stream set up conveys the more volatile part of the residue to the cold finger and schradan (v.p. 2.46×10^{-4} mm at 25° C) can be separated. The schradan residues are transferred to a Kjeldahl flask, 5 ml of 10 *N* H_2SO_4 and 0.3 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are added, and the mixture is evaporated until fumes appear. Evaporation is repeated twice after the addition of a little water. The residue is diluted with a small quant. of water and the colourless phosphate solution is assayed by a method based on that of Berenblum and Chain, the extinction being measured at 735 μ . Recoveries and blanks are satisfactory. S.C.I. ABSTR.

2905. Determining traces of tetramethylphosphorodiamidic fluoride (dimefox) in crops. L. F. Dupé, D. F. Heath and I. K. H. Otter (Fisons Pest Control, Ltd., Chesterford Park Res. Sta., Essex, England). *J. Agric. Food Chem.*, 1956, 4 (3), 233-236.—The most general method consists in macerating a sample of the crop (50 g) with water, filtering, extracting the filtrate with CHCl_3 , evaporating to low bulk, transferring the residue to a micro-distillation apparatus, and distilling in the presence of a few drops of glycerol-ethanediol mixture. The dimefox in the distillate is estimated as phosphate by the method of Berenblum and Chain; the sensitivity of this method is 0.02 p.p.m. of dimefox on a 50-g sample. A second method, used for oily crops, e.g., cocoa beans, consists in distilling a macerate in oil and separating the dimefox from interfering compounds in the oily distillate. The methods described gave satisfactory low blanks on 15 crop samples and reproducible recoveries on 10 crops further studied. S.C.I. ABSTR.

See also Abstract 2711.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2906. Boiling flasks (narrow-necked), conical, flat bottom and round bottom. British Standards Institution (2 Park St., London). B.S. 2734:1956, 7 pp.—Ranges of narrow-necked boiling flasks suitable for normal laboratory use are specified, and recommendations are given for material, dimensions and construction. O. M. WHITTON

2907. Addendum to apparatus for the determination of fluorine by distillation. E. Tiedemann (Victor Chem. Works, Castrop-Rauxel, Germany). *Z. anal. Chem.*, 1956, 150 (1), 1-2.—In the determination of F by distillation in the apparatus previously described (*Anal. Abstr.*, 1956, 3, 402), entrainment of acid is avoided by inclusion of perforated glass plates in the distillation-head, which then acts as combined fractionation- and splash-head. J. P. STERN

2908. Table suitable for mounting a microchemical balance. A. Steyermark, E. D. Ingalls and J. W. Wilkenfeldt (Hoffmann-La Roche Inc., Nutley, N.J., U.S.A.). *Anal. Chem.*, 1956, 28 (4, Part 1), 517-520.—A table suitable for mounting a microbalance where vibrational disturbances are encountered is described. It comprises essentially a reinforced concrete block on deflected springs and

is shown to have an isolation efficiency of about 93 per cent. Ten balances mounted on such tables had precisions ranging from 1.1 to 2.6 μg , although they were located on a floor above a manufacturing area.

K. A. PROCTOR

2909. A microgram balance with jewel bearing. E. Hess and W. Thomas. *Z. angew. Phys.*, 1955, 7 (12), 559-562.—The beam balance described takes a maximum load of 500 mg and has a sensitivity of 1111 mm per mg unloaded and 909 mm per mg at maximum load with corresponding periods of oscillation of 15 and 14 sec.

PHYS. ABSTR.

2910. Determination of the moisture content of materials [e.g., tobacco, moving continuously or intermittently on a conveyor belt]. Industrial Machinery Co. Ltd. (Inventor: S. Gilman) (22-24 Corsham Street, London). Brit. Pat. 745,917; Date Appl. 24.2.53.—The wt. per unit area of the material is measured by a suitably positioned radiation gauge (β -ray gauge) while a second gauge measures one or more of the electrical characteristics of the material that are affected by moisture, e.g., the dielectric properties or the electrical resistance. The electrical outputs of the two gauges are fed to an electronic circuit which operates to provide an indication of the percentage moisture content of the material.

J. M. JACOBS

2911. A simple method for the direct recording of extinction curves in the evaluation of chromatograms. N. Grubhofer (Inst. f. Virusforsch., Heidelberg). *Z. Naturforsch.*, 1956, 11b (1), 44-46.—The stained section of the filter-paper is placed in the path of light impinging on a photocell and the current generated in the cell causes movement of a mirror galvanometer. The light beam reflected from the mirror galvanometer is reflected by a mirror with a curvature such that it converts the extinction values to a linear scale. The movements of the light spot can be watched on a ground glass screen, and by using transparent paper the extinction curve can be plotted straight on to the paper. The method for calculating the correct curvature of the mirror is described.

E. KAWERAU

2912. Gas-liquid chromatography: the gas-density meter, a new apparatus for the detection of vapours in flowing gas streams. A. J. P. Martin and A. T. James (Nat. Inst. for Med. Res., Mill Hill, London). *Biochem. J.*, 1956, 63 (1), 138-143.—A very sensitive gas-density meter is described. It can be used for the detection of vapour in gas streams, and is suitable for use with the gas-liquid chromatogram.

J. N. ASHLEY

2913. Use of cinematography for studying paper chromatography. J. Dixmier, P. Dupuis and M. Nortz. *Chim. Anal.*, 1956, 38 (4), 129-133.—The course of the development of a paper chromatogram can be followed by filming at a low speed. For example, if a chromatogram during its development is photographed every min. over a period of 12 hr., the final film will last for 45 sec. In this way, details such as the manner of the flow of the solvent or the spread of the spots can be observed, details that otherwise might pass unnoticed because of the low rate of development.

J. H. WATON

2914. The Leib permanent viscometer. O. Leib (Engelschalking Str. 67, Munich, Germany). *Erdöl u. Kohle*, 1955, 8 (12), 899-900.—The oil under test flows from the conical bottom of a

constant-level reservoir through a short capillary into a similar but deeper vessel (A) from the bottom of which it flows through a longer capillary of the same bore. The level (h) built up in A when the flow rates are equal is a measure of the kinematic viscosity ν . The dynamic viscosity $\eta = \nu d$ is found by bubbling air through the oil in A; the pressure required to do this (hd) can be read on a gauge calibrated in centipoises, and will also operate a recorder or regulating device. The capillary dimensions must be chosen within a range, which is shown graphically, over which the linear relation of ν and h holds. The accuracy depends primarily on the reading of the height of the oil column or the pressure of the air supply.

A. R. PEARSON

2915. Microviscometer. M. Freund and A. Vámos (Hungarian Petr. and Nat. Gas Res. Inst., Budapest). *Erdöl u. Kohle*, 1955, 8 (12), 895-898.—A thread of oil <4 cm long (≈ 30 mg) is timed while it flows under gravity down the vertical capillary leg of a U-tube, between two marks 11.5 cm apart. The first timing is rejected because capillary effects at the front and rear of the thread are not balanced. The thread is drawn up again at the same speed and several such timings are made. The flow is laminar with no kinetic correction, so that the Poiseuille equation applies, and since the sample flows under its own weight the equation can be simplified to $\nu = gr^2/8l$ centistokes, where ν is the kinematic viscosity, g is the gravitational constant, r is the radius of the capillary (0.025 to 0.25 mm), and l is the time taken to flow l cm. The instrument can be used for absolute measurements if a capillary of uniform bore is available, but normally an instrumental constant is determined by testing oils of known ν . The results agree within ± 1 per cent. with those of the Ostwald viscometer.

A. R. PEARSON

2916. Low-temperature laboratory centrifuge. L. Riccobini, N. Fochi, E. Ferrari and G. Tagliavini (Inst. Phys. Chem., Univ. Modena, Italy). *Chim. e Ind.*, 1956, 38 (1), 11-14.—A laboratory centrifuge for use between -20° and -70° C, with an accuracy of $\pm 1.5^\circ$ C, is described. Full working diagrams of the apparatus are given, together with detailed circuits of the thermal and rotary controls, including a thermoregulator in which a thermistor and gas-filled tetrode circuit are used.

C. A. FINCH

See also Abstracts 2613, 2736.

Optical

2917. The problem of co-solutes ('partners') in flame spectrophotometry. J. Fischer and A. Doiwa (Inst. f. anorg. Chem., Metallges. A.-G., Frankfurt am Main, Germany). *Mikrochim. Acta*, 1956, (1-3), 353-361.—The reproducibility of flame-photometry methods, which are excellent for mixtures of alkalis, depends largely on the influence of co-solutes. Secondary interferences such as stray light and alteration of the atomising conditions can readily be eliminated. The real effects of co-solutes on dissociation and ionisation in the flame are discussed; in some cases they result in suppression and in other cases enhancement of the emission of the sought elements. Flame temperature and concentration of the solution can each exert considerable influence which may vary for different alkaline elements present in the solution being analysed.

D. F. PHILLIPS

2918. Filter system for radioactive exhaust from flame spectrophotometer. J. H. Edgerton, H. G. Davis, L. C. Henley and M. T. Kelley (Anal. Chem. Div., Oak Ridge Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 557.—A filter system with a special filter unit of asbestos-impregnated paper and an exhaust fan is described for use with the Beckman model B flame spectrophotometer when radioactive soln. are being analysed. New calibration curves have to be prepared when the system is first put into operation.

K. A. PROCTOR

2919. The precision of the cathode arc layer method. G. Holdt (Max Planck Inst. f. Metallforsch., Stuttgart, Germany). *Mikrochim. Acta*, 1956, (1-3), 311-318.—In using the cathode arc layer technique, irregular consumption of the cathode can cause variations in line and background intensities. It is shown that by use of a rotating cathode (100 r.p.m.) these fluctuations are considerably reduced. Optimum spectrographing conditions are stated. The sample is diluted with five times its weight of pure graphite. The overall assessment of any particular procedure is obtained by means of easily prepared intensity-fluctuation diagrams.

D. F. PHILLIPS

2920. A metal capillary electrode for the direct spectrographic investigation of solutions. H. J. Eichhoff and K. Picard (Inorg. Chem. Inst., Univ. Mainz, Germany). *Spectrochim. Acta*, 1956, **7** (6), 396-397.—In the electrode system described, the lower electrode has a hemispherical tip from which a capillary tube leads downwards to a slotted cavity for holding the solution; the upper electrode is conical.

D. G. HIGGS

2921. Oxidation reactions during sparking. A. Keil (Lab. Platinschmelze Dr. E. Dürrwächter, Pforzheim, Germany). *Spectrochim. Acta*, 1956, **7** (6), 367-372.—Evidence is given to show that the spectrographic sparking of a silver surface produces an oxide film, which in certain circumstances may alter the total brightness of the spark and also the relative intensities of the alloy elements. For silver alloys the sparking-off effects depend on whether the alloy elements are in true solid solution or are present as segregated oxides in the form of intercrystalline films, as has been shown with cadmium and manganese. In either case the spectra tend to reach similar conditions after long sparking.

D. G. HIGGS

2922. Contrast changes in Eastman Kodak spectrum analysis No. 1 emulsion during cold storage, and their effect on observed intensity ratios. C. Feldman and J. Y. Ellenburg (Oak Ridge Nat. Lab., Oak Ridge, Tennessee, U.S.A.). *Spectrochim. Acta*, 1956, **7** (6), 349-357.—Carefully controlled tests have indicated that the Eastman Kodak SAI emulsion undergoes a 0 to 4 per cent. decrease in contrast at various wavelengths when stored for a period of 1 year at -17.8°C (0°F), and a 4 to 12 per cent. increase in contrast when stored for a similar period at 4.4°C (40°F).

D. G. HIGGS

2923. Expanded cuvette holder for model DU spectrophotometer. G. C. Riggie (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Rev. Sci. Instrum.*, 1956, **27** (3), 175-176.—An expanded cell holder which will hold 10 cells is briefly described.

G. SKIRROW

2924. Improvements relating to refractometers. National Research Development Corp. (1, Tilney Street, London) (Inventor: I. G. Austin). Brit. Pat. 748,350; Date appl. 29.4.53.—An interference refractometer, of particular use with gaseous media, one of which is air and the other a gas or vapour, comprises an elongated box for containing the gas or vapour. Two beams of light from a single source, defined by a pair of slits, pass through the air and the gas or vapour, which are separated by the plane diaphragm constituted by one long wall of the box. The beams are finally caused to converge to a point, e.g., by means of a converging lens. Since the separation of the two beams is only a little greater than the thickness of the diaphragm, it is possible to ensure that the separations of the interference bands are great enough for high magnification to be unnecessary. The length of the box is made only so great as to give a maximum interference pattern shift, for a given range of refractive index, of not more than about three times the central white band of the interference pattern. The fringe shift is measured directly on a graduated scale contained in the low-power eyepiece.

J. M. JACOBS

2925. The electron microscope in analysis. T. Reis. *Chim. Anal.*, 1956, **38** (4), 115-124; (5), 161-170.—The possibilities and limitations of the electron microscope are discussed, and the directions are indicated in which improvements are being made. When the electron microscope is combined with a micro-analyser, it is possible to detect the presence of certain elements in the sample in amounts as low as 10^{-14} to 10^{-16} g. Their presence is revealed by peaks in the electron spectrum after the passage of electrons through the sample. Examples of the application of electron microscopy are discussed, including the preparation of samples, the formation of metallic films by evaporation in vacuum, the measurement of the size and shape of small particles (e.g., carbon black), and the examination of surfaces, particularly in relation to the determination of the molecular weights of silicones.

J. H. WATON

2926. Recording nickel carbonyl detector. J. E. McCarley, R. S. Saltzman and R. H. Osborn (Hercules Expt. Sta., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 880-882.—A sensitive, continuously recording instrument for detecting nickel carbonyl in the air is described. A stream of air (500 ml per min.) flows through a nozzle and impinges on a hot borosilicate-glass disc, on which nickel carbonyl, if present, is deposited. A collimated beam of plane-polarised light falls on the disc at the Brewsterian angle for borosilicate glass, its plane of polarisation being perpendicular to the plane of incidence. This arrangement results in extinction, so that no light is reflected from the disc until a deposit is formed. The intensity of the reflected light is then measured by a recording photomultiplier photometer calibrated in p.p.m. of nickel carbonyl. Conc'n. in the range 0.05 to 4 p.p.m. by vol. can be measured, and at a conc'n. of 1 p.p.m. the accuracy is ± 0.2 p.p.m. The detector is also sensitive to iron carbonyl and can presumably be used for other metallo-organic vapours and gases such as tetraethyl-lead.

K. A. PROCTOR

Thermal

2927. Reference thermometers for field use. British Standards Institution (2, Park Street, London). B.S. 2736:1956, 7 pp.—Requirements

are specified for reference thermometers for ordinary and tropical use suitable for determining the scale errors of other thermometers by comparison in a water bath. The thermometer is of the mercury-in-glass solid-stem type, filled with inert gas at a suitable pressure, and is calibrated for total immersion. O. M. WHITTON

2928. Electronic conversion for graphic recording with the Chevenard photographically recording thermobalance. S. Gordon and C. Campbell (Pyrotechnics Chem. Res. Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 124-126.—A simple and relatively inexpensive apparatus is described which gives a pen-and-ink record of thermogravimetric curves with a potentiometric-type recorder. This is accomplished by means of a linear variable differential transformer, used as a transducer, which converts the balance-beam displacements to electrical energy. The minimum of modification to the balance is necessary. D. G. HIGGS

See also Abstract 2754.

Electrical

2929. Modified Joliot apparatus for study of the electro-deposition of radioactive materials. W. H. Power and J. W. Heyd (Mound Lab., Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 523-525.—A modification of Joliot's method (*J. Chim. Phys.*, 1930, **27**, 119) of detecting deposition of a radioactive material without interference from inactive decomposition products is described. The modification allows the potential of a radiation-transparent electrode to be uniformly varied, and the ionisation current in the vicinity of the electrode to be continuously recorded. Deposition of the radioactive element is detected by an increased ionisation current record of an ionisation chamber adjacent to the electrode, and dissolution of the deposit by a decrease in the ionisation current. A variable electronic potential controller is used to control the cathode or anode potential. The use of the apparatus for recording deposition and dissolution potentials of Po in 4.7 N HCl is described. K. A. PROCTOR

2930. Continuous zone electrophoresis by crossed velocity fields in a supporting medium. I. The electric control of the fractionation process. I. Brattsten [and L. Lannefors] (Inst. Biochem., Univ. Uppsala, Sweden). *Ark. Kemi*, 1955, **8** (3), 205-226.—The efficiency of continuous fractionation by crossed electric and hydrodynamic flow fields (Svensson and Brattsten, *Brit. Abstr. C*, 1950, 431; Grassman and Hannig, *Angew. Chem.*, 1950, **62**, 170) depends on the control of factors that cause remixing of the separating substances. The hydrodynamic velocity is sensitive to changes in the speed of the pump transporting liquid through the cell, so that the motor must be run from a const. voltage source. Both electric velocities and heat transfer can be controlled by stabilisation of the bath current. Suitable devices for controlling these factors are described in an appendix (by L. Lannefors).

II. Fractionation of protein mixtures and a description of the cuvette. I. Brattsten. *Ibid.*, 1955, **8** (3), 227-244.—Details of the construction of a new cuvette for use with this method are given. To obtain a uniform mobility distribution in the separation zone this is supplied with a dilute buffer soln. of uniform conductivity and an ionic

strength of 0.05 to 0.03; between this zone and the electrode compartments, end zones of more conc. soln. are inserted. The end zones act as a barrier to the migration of foreign ions into the separation zone and also facilitate exchange of ions with the electrode compartments. Fractionation expt. with the proteins of normal and pathological sera, normal cerebrospinal fluid and algae are described and discussed. H. F. W. KIRKPATRICK

2931. Rapid automatic scanning device for paper electrophoresis and chromatography. D. Z. Silver and R. Bookman (The George Pines, M.D. Allergy Group, Beverly Hills, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 558.—An attachment to the Beckman model B spectrophotometer to give rapid automatic scanning of paper-electrophoretic strips and of paper chromatograms (maximum width 1 inch) is described. No pre-treatment of the paper strips is necessary whatever the type of paper used. The output of the spectrophotometer is connected to a chart recorder and the values of areas under the curves thus obtained can be determined with a planimeter, by rough visual comparison, or by cutting and weighing the comparative areas. K. A. PROCTOR

2932. Evaluation of paper chromatograms by direct polarographic scanning. A. Langer (Westinghouse Res. Lab., E. Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 426-427.—A simple apparatus in which amalgamated gold wire is used as the polarisable electrode is described for the direct polarographic scanning of paper chromatograms. The procedure is applicable to inorganic ions and organic substances which can be evaluated polarographically. Nitrobenzene, nitrotoluene and other nitro compounds in alcohol-water soln. have been scanned successfully. K. A. PROCTOR

2933. Electrophoresis cells modified for determination of labelled protein fractions. R. E. Hein, R. E. Clegg, T. J. Clark and R. H. McFarland (Kansas State Coll., Manhattan, Kan., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 544-545.—The modification of the ascending arm of the centre cell of a Tiselius electrophoretic apparatus to measure the radioactivity associated with labelled (^{32}P , ^{45}Ca , ^{35}S , ^{14}C) protein fractions is described. The modification does not affect electrophoretic patterns, protein mobilities or the concn. of the separated protein fractions. K. A. PROCTOR

2934. Differential polarography with an electronic recording integro-differentiating polarograph. S. B. Tsfasman (Central Lab. of Automatics, Min. Ferrous Metallurgy, USSR). *Zavod. Lab.*, 1956, **22** (2), 131-140.—A recording polarograph suitable for both normal and differential (derivative) polarography is described. For multicomponent solutions, multicomponent standard solutions are recommended. G. S. SMITH

2935. Increase in sensitivity of a polarographic determination on the dropping-mercury electrode. V. S. Fikhtengol'ts (Leningrad Sci. Res. Inst. of Labour Hygiene and Professional Diseases). *Zavod. Lab.*, 1956, **22** (2), 140-146.—A method of increasing polarographic sensitivity, based on the forcing of the break-off of drops from the dropping-mercury electrode and the use of a special galvanometer shunt, is described. G. S. SMITH

2936. Automatic iR drop compensator for polarographic use. W. Jackson, jun., and P. J. Elving [Standard Oil Co. (Ohio), Cleveland, Ohio, U.S.A.]. *Anal. Chem.*, 1956, **28** (3), 378-381.—An automatic device is described which eliminates manual iR (internal resistance) corrections by inserting into the circuit a continuously compensating source of potential, equal and opposite to the iR drop in the circuit. The device can be used in conjunction with any conventional type of polarograph and is useful in the examination of soln. with high electrical resistance. The compensator has been used with dropping-mercury electrodes and solid electrodes for both reduction and oxidation processes. Reproducibility and accuracy are stated to be within the limits of normal polarographic analysis.

K. A. PROCTOR

2937. Improvements in glass electrodes. George Kent, Ltd. (199, High Holborn, London) (Inventor: C. Chalmers). Brit. Pat. 748,506; Date appl. 16.6.53.—In glass electrodes for use at high temperatures (e.g., 50° to 100° C), leaching of the glass stem, which causes error in the measured pH values, is prevented by rendering the inner surface of the stem-tube water-repellent by coating it with a suitable org. compound, e.g., an alkyl siloxane.

J. M. JACOBS

2938. Potentiometric neutralisation titrations in non-aqueous media with bimetallic electrodes. V. Novák (Výzkumný ústav org. syntesy, Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 848-853.—New bimetallic electrode systems for potentiometric neutralisation titrations in anhyd. methanol and glacial acetic acid are described. For titrations with the former solvent, the bimetallic system Pt-Ag is best, but the systems W-Ag, Te-Ag, W-graphite, Pt-Au, W-Au and Pt-graphite are likewise suitable. For titrations in acetic acid (containing 30 per cent. of acetic anhydride), electrodes consisting of graphite and one of the following metals have been used successfully—W, Au, Sb, Ag, Pt or Te.

G. GLASER

2939. Potentiometric neutralisation titrations with bimetallic electrode systems. V. Novák (Výzkumný ústav org. syntesy, Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1955, **49** (6), 934-936.—The dependence of the e.m.f. of the following 12 electrodes on the pH has been studied (the numbers give the ratio $\Delta E/\Delta pH$ in mV)—Pt-Ag, 58; Pt-Au, 42; Pt-graphite, 40; Sb-Ag, 68; Sb-Au, 43; Sb-graphite, 43; Te-Ag, 58; Te-Au, 41; Te-graphite, 43; W-Ag, 56; W-Au, 35; W-graphite, 40. The e.m.f. of the pairs with a silver electrode is a linear function of pH in the pH range from 3 to 8 only; they are therefore suitable for the titrations of strong and weak bases and strong acids, but not of weak acids. The e.m.f. of the remaining electrode systems exhibits a continuous, practically linear, dependence on pH throughout the entire pH range, and can therefore be used for the titration of weak acids as well. The systems Te-Ag, Te-Au, Te-graphite, Sb-Ag and Sb-Au have hitherto not been described in the literature.

G. GLASER

2940. Oxidation of platinum electrodes in potentiometric redox titrations. J. W. Ross and I. Shain

(Univ. of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (4, Part 1), 548-551.—The oxidation of the surface of platinum electrodes in potentiometric redox titrations can explain the drifting potentials often observed. The concn. and nature of the oxidising and reducing agents present in the soln. affect the formation and dissolution of the oxide coating, both of which are slow processes. Automatically recorded titration curves show an end-point error consistent with the drifting of potentials studied with the aid of potential-time curves.

K. A. PROCTOR

2941. Devices for automatic potentiometric titration. R. Audran and D. T. R. Dighton (Kodak Ltd., Harrow, Middlesex, England). *J. Sci. Instrum.*, 1956, **33** (3), 92-95.—Two automatic titration devices are described. Both operate by allowing a comparatively high rate of delivery from the burette until the electrode potential is about 100 mV from the equivalence potential; then the tap practically closes giving a low rate of flow which ceases at the equivalence point. The first device, in which an electronic valve amplifier is used, is adaptable to any titration whose end-point can be determined potentiometrically. The second device, which makes use of a sensitive relay, is suitable only when the electrode has a low internal resistance.

G. SKIRROW

2942. Analytical applications of the rotated platinum-wire electrode. I. M. Kolthoff (Univ. Minnesota, Minneapolis, Minn., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (1), 47-49.—The method is usually applicable to concn. of $\geq 10^{-5}$ N. Oxygen can be determined amperometrically in water, gases and biological media; I, Ti and Pb can be determined in small quantities. Mercaptans (10^{-5} N), Cl^- (10^{-4} N) and I^- (10^{-3} N) can be determined by amperometric titration with $AgNO_3$. Other applications include the determination of As^{III} , Sb^{III} and Sn^{II} by oxidation with Br and of NH_3 by oxidation with OBr^- .

A. A. ELDRIDGE

2943. High-frequency instrumentation. J. C. Clayton, J. F. Hazel, W. M. McNabb and G. L. Schnable (Univ. of Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (3), 269-279.—The effect of cell parameters on the sensitivity of high-frequency titration cells was studied in instruments responding to changes in either effective capacitance or effective conductance. A cell that minimises the effect of the dielectric const. of the soln. and responds only to conductance is described. Progressive variation of the distance (1.5 to 60 cm) between the electrodes, or the diameter (3 to 13 mm) of the cell, shifts the regions of useful concn. of the response curves. Increasing the length (2.5 to 12.5 cm) of the metal electrodes, or decreasing the thickness from 3.9 to 2.5 mm, extends the effective concn. regions. An equation is derived relating the specific conductance of the soln. of the sample to the dimensions of a cell having max. sensitivity. Constant-temp. ($\pm 0.1^\circ C$) systems permitting aq. and non-aq. liquids to be used as circulating media are described briefly.

W. J. BAKER

See also Abstract 2750.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	millicurie	mC
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicron	mμ
aqueous	aq.	millivolt	mV
atmospher, -e, -ic	atm.	minimum	min.
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul -e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	number	no.
coefficient	coeff.	observed	(obs.)
concentrated	conc.	ounce	oz
concentration	concn.	part	pt.
critical	crit.	patent	pat.
crystalline	} cryst.	parts per million	p.p.m.
crystallised		per cent. wt. in wt.	per cent. w/w
cubic	cu.	per cent. wt. in vol.	per cent. w/v
current density	c.d.	per cent. vol. in vol.	per cent. v/v
cycles per second	c.p.s.	potential difference	p.d.
decompos -ing, -ition	(decomp.)	pound	lb
density	ρ	precipitate	ppt.
density, relative	d or wt. per ml	precipitated	pptd.
derivative	deriv.	precipitating	pptg.
dilute	dil.	precipitation	pptn.
direct current	d.c.	preparation	prep.
distilled	dist.	qualitative, -ly	qual.
electromotive force	e.m.f.	quantitative, -ly	quant.
electron-volt	eV	recrystallised	recryst.
equivalent	equiv.	refractive index	n_D^{20}
experiment	expt.	relative humidity	R.H.
foot, feet	ft.	revolutions per minute	r.p.m.
gram	g	saponification value	sap. val.
gram-molecule	mole	saturated calomel electrode	S.C.E.
half-wave potential	$E_{1/2}$	second (time)	sec.
horse-power	h.p.	soluble	sol.
hour	hr.	solution	soln.
hydrogen ion concentration [H ⁺]	[H ⁺]	specific gravity	sp. gr.
hydrogen ion exponent	pH	specific rotation	$[\alpha]$
inch	in.	square centimetre	sq. cm
infra-red	i.r.	standard temperature and pressure	s.t.p.
insoluble	insol.	temperature	temp.
kilogram	kg	ultra-violet	u.v.
kilovolt	kV	vapour density	v.d.
kilowatt	kW	vapour pressure	v.p.
maxim -um, -a	max.	volt	V
melting-point	m.p.	volume	vol.
microcurie	μC	watt	W
microgram	μg	wavelength	λ
microlitre	μl	weight	wt.
micron	μ		
milliampere	mA		

In addition the following symbols are used—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	N

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicals are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu⁺⁺, Al⁺⁺⁺, Cl⁻, SO₄⁼⁻. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

ANALYTICAL ABSTRACTS

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